

COLLINGWOOD HARBOUR

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REMEDIAL ACTION PLAN



MEETING BIOLOGICAL AND CHEMICAL TARGETS
FOR SEDIMENT QUALITY IN
COLLINGWOOD HARBOUR, 1988-1993

ENVIRONMENTAL STATUS REPORT

JANUARY 1994

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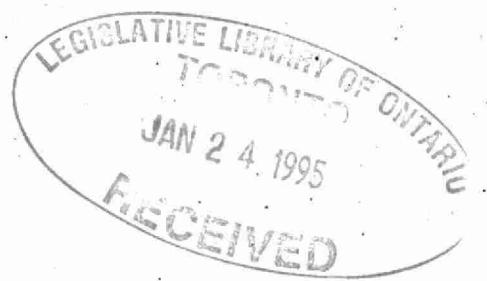
ENVIRONMENTAL STATUS REPORT #1

MEETING BIOLOGICAL AND CHEMICAL TARGETS FOR SEDIMENT QUALITY IN COLLINGWOOD HARBOUR

1988 - 1993

REPORT PREPARED BY:

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Ontario Ministry of Environment and Energy
January 1994**



PREFACE

This report has been prepared under the auspices of the Great Lakes Remedial Action Plan Program.

Financial support for the investigation was provided by the Ontario Ministry of Environment and Energy and Environment Canada.

The report is the first in a series of environmental status reports conducted in support of delisting Collingwood Harbour and an Area of Concern, and was written by G. Krantzberg, Collingwood Harbour RAP Coordinator, Ontario Ministry of Environment and Energy.

The report presents the findings and conclusions of the author and does not necessarily represent the view or policies of the sponsoring agencies.

FOREWORD

Since designation of Collingwood Harbour as an Area of Concern in 1977, the Collingwood Harbour Remedial Action Plan (RAP) has been working towards ways of addressing and correcting the harbour's environmental problems. The fundamental goal of the Collingwood Harbour RAP continues to be the improvement and protection of the quality of Collingwood Harbour's ecosystem. In consultation with the community, the Public Advisory Committee (PAC) has identified goals and uses for the harbour, and is implementing a strategy for ecosystem recovery to delist Collingwood Harbour as an Area of Concern.

Environmental conditions that detract from the goals and uses are the primary concern of the RAP. While water quality has improved substantially over the past decade, sediment contamination from historical industrial activities is a potential concern. Bioassessment of Collingwood Harbour in 1986, included *in situ* algae, fish, and laboratory studies on fish and benthic invertebrates. The current report summarizes findings from investigations conducted from 1988 to 1993. The emphasis was on determining whether trace organic or metal contaminants were present in concentrations and physicochemical forms to impair aquatic biota.

The findings of this report will be included in the Stage 3 document, in the evaluation of delisting targets.

EXECUTIVE SUMMARY

Currently, the significance of metal residues in biota and the effects of contaminants in sediment on organism health are not easily predicted in cases where sediment contamination is considered to be marginal. Comparisons of biotic responses and tissue residues in exposed organisms with those of organisms from locations remote from pollutant sources is a means of identifying adverse biological effects. In the case of Collingwood Harbour, tissue residues of contaminants in field and laboratory organisms were comparable to concentrations observed in organisms colonizing uncontaminated sediment. Sediment bioassessment revealed no significant mortality, and growth of test organisms exposed to harbour sediment equalled or exceeded that of reference values. Sediment bioassays using sensitive endpoints indicate no observable impacts of harbour sediment on the biota, however, *Tubifex tubifex* reproduction was impaired in sediment from the Collingwood Shipyards.

With the exception of the Collingwood Shipyards, the bioassay information, coupled with field observation on native benthic invertebrates, young of the year spottail shiners, sport fish and introduced mussels provides multiple lines of evidence that support the conclusion that concentrations of biologically available contaminants in Collingwood Harbour sediment are not of toxicological significance. In the CSL property and proximity, a program to remove sediment that elicited adverse biological responses began in November 1992 and concluded in November 1993. The program

coupled sediment removal with the opportunity to demonstrate new innovative technology that could have potential for sediment rehabilitation in more seriously contaminated areas throughout the Great Lakes.

INTRODUCTION:

Contaminants in sediment throughout the nearshore of the Great Lakes frequently exceed the Ontario Ministry of Environment and Energy (MOEE) sediment management guidelines (Persaud et al. 1992) which identify the Lowest Effect Level (LEL), the concentration at which 5% of benthic invertebrates are anticipated to suffer adverse effects. According to the guidelines, biological testing is required to determine whether exceeding this level has adverse implications for the health of aquatic organisms. In some instances, inorganic and organic trace contaminants approach or exceed the Severe Effect Level (SEL). In general, this level cannot be tolerated by 95% of macrobenthic species. Concentrations of contaminants in Great Lakes sediment frequently exceed the LEL, and are above the SEL, particularly in Great Lakes Areas of Concern (Painter 1992).

The guidelines are based on the total amount of metal that can be removed from sediment particles without dissolving the crystalline matrix of the particles. Analyses of metal concentrations in sediment using hot, concentrated acids , however, have been shown to be limited in use for predicting site-specific environmental effects on organisms. Biological and environmental factors influence metal bioavailability and, consequently, metal toxicity. It has been clearly demonstrated that the biogeochemistry and the physicochemical environment affect the forms of and

subsequent biological availability of contaminants (Luoma 1983, Campbell and Tessier 1989, Davis-Colley et al 1985, Campbell et al 1988, Krantzberg and Stokes 1988). As a consequence, biological tests are an essential means of evaluating environmental threats due to the presence of pollutants, when chemical measurements suggest there is a potential for adverse ecological consequences (Chapman 1989, Landner 1988, International Joint Commission 1988, van Veen and Stortelder 1988, Krantzberg and Bailey 1983, Karr 1987, Persaud et al 1992, Burton 1991).

STUDY APPROACH

From 1986 to 1993, a series of investigations assessed the biological consequences of contaminants in sediment from Collingwood Harbour. In 1986, acute sediment bioassays using mayfly nymphs (*Hexagenia limbata*) and juvenile fathead minnows (*Pimephales promelas*) demonstrated that sediment from the Harbour was not lethal during 10 day (acute) exposure intervals (Krantzberg et al 1989). In a limited number of samples, however, lead residues in bioassay organisms were elevated relative to controls, resident infauna, and introduced mussels. While mortality was not observed, the question of elevated Pb residues in test organisms and potential for chronic sublethal toxicity was apparent. Due to the bioassay protocol used at that time, it was unclear as to whether the apparently anomalous results were due to artifacts associated with the test methods, exposure time and sediment collection techniques,

or whether sublethal toxicological properties of the sediment were a potential threat to benthic organisms.

Sediment bioassays and core profiles

In November 1988 sediment collection was repeated at the two 1986 stations where bioaccumulation of metals was significantly greater than reference organisms. The bioassay design revised in order to address several hypotheses, as follows:

The 1986 sediment bioassay was conducted using the entire contents of replicate ponar grabs which were homogenized and air sieved through a 2 mm mesh prior to bioassay assembly. Tests run with surficial sediment could yield different responses.

- (a) The first hypothesis tested whether deeper sediment was more contaminated than surficial sediment. If this was the case, native infauna and introduced biomonitor would be exposed to cleaner surficial sediment than were the laboratory bioassay organisms, tested on a composite of surficial and deeper material.

The 1986 bioassay organisms were two year old mayfly nymphs and 4 to 5 month old juvenile fathead minnows, the latter weighing approximately one

gram wet weight per individual. Acute exposures were 10 day static beaker tests with mortality and bioaccumulation as the endpoints.

- (b) An alternate or additional hypothesis tested that organisms at this stage of development were not sufficiently sensitive to detect sublethal effects of contaminants. Sublethal endpoints such as growth are more responsive indicators of low level toxicity than mortality.

The 1988 study examined the combined importance of bioassay duration, organisms sensitivity (by using younger life stages), and surficial as opposed to bulk sediment chemistry for three endpoints; growth, mortality and bioaccumulation.

A second component to the study was to evaluate vertical and horizontal contaminant profiles in sediment to verify whether deeper sediment contained higher concentrations of pollutants due to historical harbour uses that have since been terminated.

- (a) Sediment cores were sectioned to a depth of 18-20 cm and analyzed at 2 cm intervals to reveal whether chemical gradients were apparent.
- (b) Additional sediment transects were situated in proximity to the confined disposal facility (CDF) and the Shipyard property, aimed at revealing the

presence or absence of chemical gradients from these two potential sources.

Mussel biomonitoring:

Mussels have been used to monitor whether contaminants in aquatic ecosystems are available to the animals inhabiting that ecosystem, and to measure the potential for those contaminants to enter the food web. Freshwater and estuarine mussels are well known for their ability to accumulate metals and have been used extensively for evaluating trace metal contamination in aquatic environments (Smith et al. 1975, Lakshmanan and Nambisan 1989, Pugsley et al 1988, Phillips 1979, Chu et al. 1990). The freshwater mussel *Elliptio complanata* has been used to monitor the bioavailability of organochlorides and polyaromatic hydrocarbons (PAH) (Heit et al. 1980, Kauss and Hamdy 1985, 1991, Innes et al. 1987).

In 1989, little data existed on the presence or biological availability of potentially toxic polyaromatic hydrocarbons (PAH) in Collingwood Harbour, particularly in the vicinity of the defunct Imperial Oil wharf location and the Goodyear outfall in Black Ash Creek. If any oil residues exist, they could contain PAH residues. In 1988, the finding of a single sediment sample that had high oil and grease concentrations in one split, and very low oil and grease concentrations in the other split (Krantzberg et al. 1989) raised additional questions as to the presence and biological reactivity of trace organic contaminants. While this anomaly may have been due to sample preparation and

analytical uncertainty, confirmation that PAH residues were not excessive was required.

As well, in 1988, the young-of-the-year spottail shiner program submitted a single sample for PAH analysis. This program samples the young-of-the-year shiners throughout the Great Lakes to identify whether contaminants are biologically available. Results obtained for this sample in 1990 indicated that tissue residues in shiners were elevated (Suns et al. 1991). The result was to be compared with the findings of the 1990 survey which used a larger sample size and complemented the mussel biomonitoring study.

The objective of this component of the investigation was to determine the need to develop remedial options for sediment in the southwestern portion of the harbour, in the vicinity of the old Imperial Oil wharf by:

- deploying caged mussels as biomonitorors of organic and inorganic contaminants
- comparing tissue residues in mussels with sediment chemistry and with tissue residues in reference organisms

1991 Benthic Community Structure:

Benthic surveys conducted in 1987 measured community composition in soft sediment predominantly in the turning basin. Disruption of the benthic community

as a consequence of dredging in 1986 was noted. Field and laboratory studies conducted after dredging, in 1988 were used to evaluate sediment associated affects on biota, including the burrowing mayfly *Hexagenia*. Local observations of high concentrations of mayflies during emergence episodes in late June and early July support the likelihood that mayfly populations colonize harbour sediment. The Collingwood Harbour Remedial Action Plan had identified the need to monitor benthic invertebrates to demonstrate that sediment supports a healthy community. This investigation was to reveal the subsequent state of recovery of harbour sediment following the dredging that occurred in 1986.

East Harbour and Shipyard Biomonitoring: Definition of biological impairment

Further study in 1992/1993 was initiated to quantify the zone of sediment, in proximity to the Shipyards, or CSL Equity Ltd. property, that exceeded provincial sediment management guidelines and failed biological testing. The objective of this final phase was to define whether a remedial action strategy was recommended, and the volume of material for which a remedial options would require development. It was decided to compare the more traditional chemical concentration guidelines with the biological approach developed by Reynoldson et al (1994).

MATERIALS AND METHODS

Sediment bioassays

Twenty-one day static sediment bioassay was conducted using mayfly nymphs and juvenile fathead minnows. Growth, mortality, and bioaccumulation of trace metals and PCBs were recorded (Krantzberg 1991a). Bioassays were conducted on sediment from stations 20, 21, and 387 (Figure 1). Both bulk and surficial sediment were collected by Shipek grab. The surface 5 cm was removed from each grab using acid-washed polyethylene spoons. Ten litres of bulk or surficial sediment were placed in plastic lined collection buckets which were then sealed, kept cold in the field, and stored at 4 °C for a maximum of two weeks. Intact sediment cores were retrieved by SCUBA divers using acid-washed and hexane- and distilled water-rinsed acrylic cores of an inner diameter of 10 cm, and surface area comparable to the test beakers.

In the laboratory, sediment was air-sieved through a 2 mm mesh to remove large particles, stones and other debris, and was then thoroughly homogenized. For the bulk and surficial sediment bioassays, 2 L glass widemouth jars, acid washed and hexane rinsed, were filled to a depth of 3 cm with sediment (surface area = 100 cm²). Dechlorinated water was gently added at a ratio of 4:1 water to sediment (v:v). Care was taken to avoid having sediments adhere to the glass above the 3 cm level. Resuspended sediment was allowed to settle for 24 hours, after which the overlying water was aerated for 1 hour by inserting airlines through the lids of the glass jars and

securing the lids in place. Water loss due to evaporation was replaced as necessary in order to maintain a water to sediment ratio of 4:1. pH and dissolved oxygen in the overlying water were monitored routinely for the duration of the experiment.

For the intact cores, overlying water was removed by siphon and replaced with dechlorinated tap water. This enhanced comparability with the beaker experiments and eliminated the potential for site water to act as a contributor to toxicity, thereby confounding the determination of sediment as a source of contaminants.

Organisms for the experimental bioassays were three to four month old juvenile fathead minnows (*Pimephales promelas*) (acquired from Ministry of Environment and Energy Rexdale laboratory cultures) weighing approximately 0.5 gm wet weight and first year mayfly nymphs (*Hexagenia limbata*) weighing approximately 30 mg wet weight, collected from a clean reference site (Honey Harbour, Georgian Bay, Ontario). Several hours prior to experimental exposure, mayflies were removed from their holding aquaria by sieving small volumes of sediment through a 500 μm mesh. Nymphs were randomly allocated to beakers containing dechlorinated water until each beaker had 10 individuals of similar size (c.a. 30 mg/ individual, wet weight). The nymphs were weighed after blotting them on acid rinsed filter papers to remove adhering water. Similarly, juvenile fathead minnows were randomly allocated to beakers containing dechlorinated water until each beaker had 10 individuals of similar size (c.a. 0.5 gms/individual, wet weight). Wet weight of each group of 10 individuals was measured using tared beakers containing 15 ml of water.

Triplicate jars for each bioassay organism were assembled and organisms were added when 24 hours of settling followed by 1 hour of aeration had elapsed. Aeration persisted for the duration of the 21 day exposure interval. All control and test jars were maintained at 20 °C by the use of a water bath and experiments were conducted at ambient light. Volume lost through evaporation was routinely replaced with dechlorinated water. During the 21 day bioassay period mortality was noted and dead organisms were removed. At day 21 organisms were removed from the bioassay jars by passing the entire contents of each jar through a 500 µm sieve and retrieving the biota. Recoveries were noted and the remaining organisms were reweighed and measured using the procedure described above. Organisms were not fed.

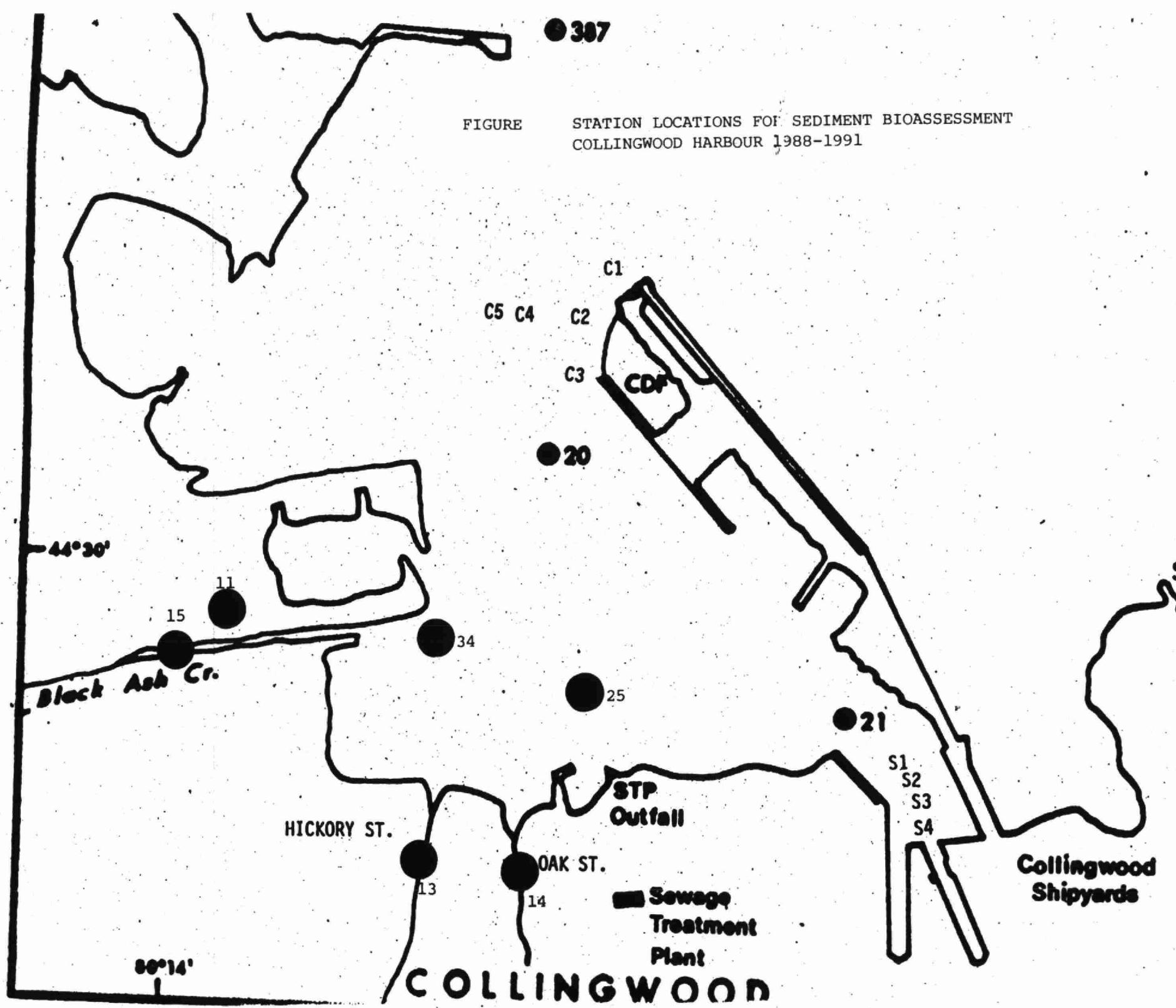
Where biomass was insufficient for metal analysis, the biota for the triplicate beakers were pooled. Minnows and mayflies were not pooled together. Sediment from Honey Harbour, from which the mayflies were collected, and Nottawasaga Bay were used as reference stations. Mortality of organisms in control sediment was not to exceed 15%, a value recognized in the literature as sufficiently low to account for organism damage due to handling, and not necessarily indicative of toxicity (ASTM 1990).

Sediment core profiles:

Cores were collected from two of the bioassay stations (stations 20 and 21) and

FIGURE

STATION LOCATIONS FOR SEDIMENT BIOASSESSMENT
COLLINGWOOD HARBOUR 1988-1991



sectioned in 2 cm intervals for metal, nutrient, and physical analysis according to Ontario Ministry of Environment and Energy (MOEE) standard protocols (MOEE 1983). In addition, sediment from one transect of 4 stations in the vicinity of the Shipyard dry dock and launch basin, and sediment from one transect of 5 stations around the perimeter of the confined disposal facility were cored to determine the extent to which contaminants were retained within both these structures (Figure 1). Duplicate cores from each station were sectioned to examine contaminant distribution with depth.

Mussel biomonitoring:

Three stations in the harbour were selected to overlap with the shiner collections, as well as to focus on potentially contaminated sites based on historical activities in the harbour. Additional locations in the creek and canals were also sampled to assess potential sources of contamination (Figure 1).

During the summer of 1990, triplicate cages containing five mussels each were submerged in the harbour at stations 21, 32 and 25, at the tributary stations 13, 14, 15 and at the Goodyear effluent confluence with Black Ash Creek. After three weeks mussels were retrieved, shucked, and three samples of four animals each were frozen on dry ice in the field and submitted to the Rexdale MOEE laboratory. The remaining animals were included in the cages as a precaution in the event of mortality.

For each sample of four mussels, two animals were individually wrapped in hexane-rinsed aluminum foil, and two animals were individually bagged in plastic "whirlpak" bags for trace organic and inorganic chemical analyses, respectively. Three samples of 4 Balsam Lake control animals were also submitted to the laboratory to measure background tissue concentrations of metals and trace organic compounds.

Duplicate sediment samples were collected concurrent with mussel retrieval. For the harbour locations, sediment was sampled by Ponar grab, and the top two to three cm were removed using plastic spoons and placed in plastic PET and amber glass sample jars for metal and organic analyses, respectively. At the tributaries, sediment was retrieved using hand held stainless steel coring devices inserted to a depth of three cm. Cores were pooled and homogenized in order to acquire sufficient material for analysis. All samples were placed in ice-filled coolers, and transported to the laboratory for analyses.

1991 Benthic Community Structure:

Five Ponar grabs were individually washed through 600 μm nitex mesh bags, ensuring that each grab was at least 1/4 filled for each sample. Benthos were washed into separate labelled jars and preserved with 10% formalin buffered with sodium borate. Samples were sorted using a dissecting microscopied and identified to the lowest taxonomical catagory possible.

At several stations additional sediment was collected by Ponar grab and sieved through 600 um "Nytex" nylon mesh bags in the field. Material retained by the sieves was transferred to clean plastic sorting trays. Two 3+ gm samples of oligochaetes were removed using pasteur pipettes and placed in separate "whirlpac" bags and frozen. Two additional 3+ gm samples of oligochaetes were transferred gently to 1 L PET bottles containing a 3 cm depth of clean sediment and topped up with harbour water. Clean loam was used for gut clearance for oligochaetes. After 24 hr at 10 °C the oligochaetes were sieved through plastic screens, removed to two duplicate whirlpak bags, and frozen. Frozen samples were returned to the laboratory for analyses.

Concurrent with biota sampling, sediment was collected by Shipek grab at each stations. The surface 2 cm were removed from each grab using acid-washed polyethylene spoons. Duplicate jars were prepared for metal, nutrient and particle size, and trace organic analyses. These samples were kept cold in the dark until submission to MOEE for analyses. Sediment pH and Eh were be measured at time of collection.

East Harbour and Shipyard Bioassessment:

In 1992/93, a final investigation was designed to define the environmental significance and extent of the sediment contamination. Twenty four stations were sampled. Three were located in the Shipyard dry dock, three in the launch basin, and

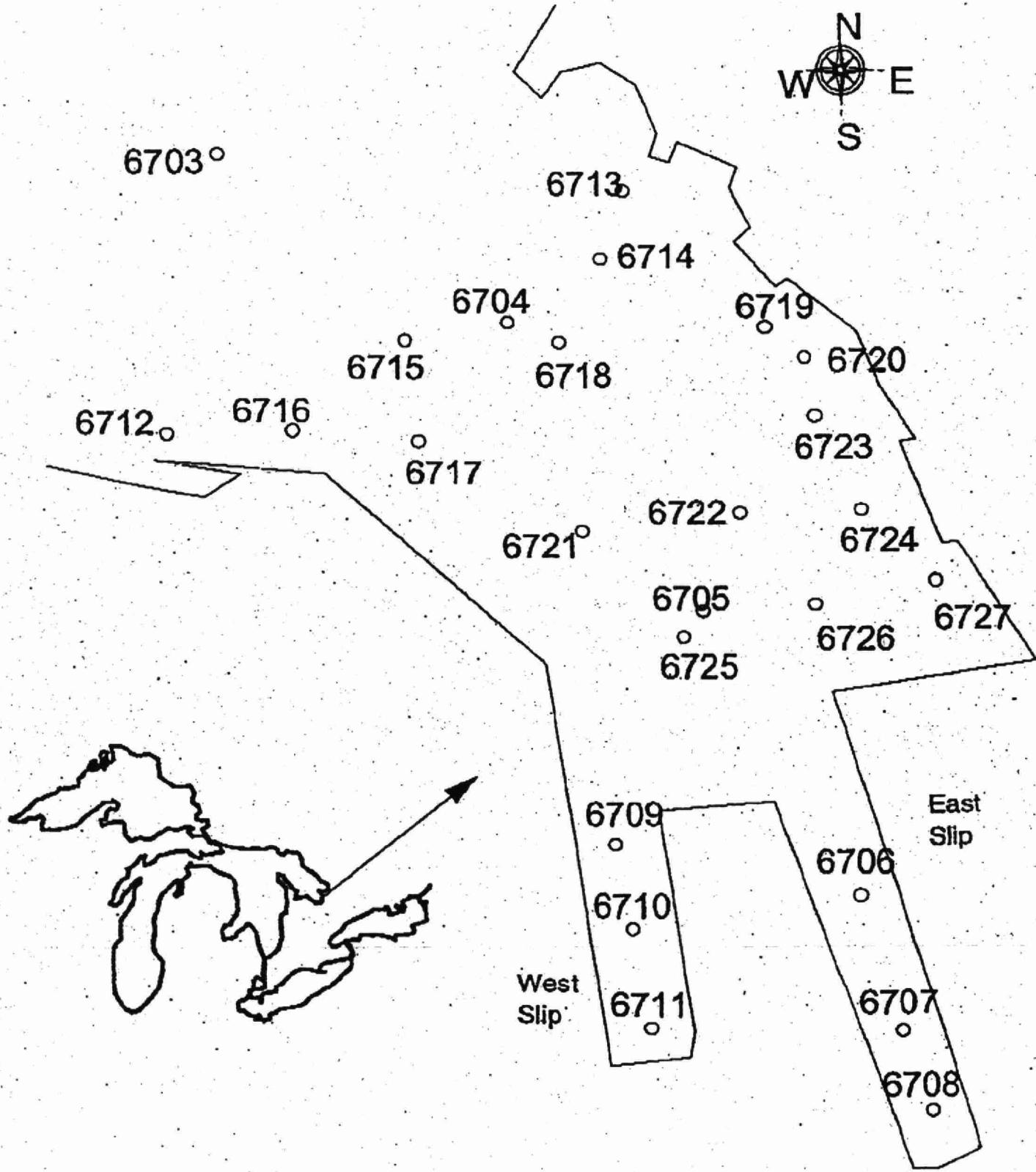
the remainder were distributed along a grid within the northeast portion of the harbour (Figure 2). Box cores were deployed for benthic community structure, and were sampled by inserting five 10 cm plexiglass tubes (i.d. 5.5 cm) into the sample. Sediment chemistry and particle size were determined by sampling the top 2 cm after tubes had been inserted and before removing the tubes. For benthic community analyses, replicates were sieved in the field through a 250 μm mesh. Sieved replicates were placed in scintillation vials and preserved with 4% formalin. After 24 h formalin was replaced by ethanol. All samples were sorted using low power on a stereo microscope. Identification was completed to the species level where possible. Taxonomic verification was conducted by referral to recent published keys, reference collections and consultation with recognized experts.

Five additional box cores or ponar grabs were taken and the upper 10 cm stored in glass containers at 4 °C until returned to the laboratory for subsequent use in sediment bioassays. Each bioassay sample was treated as a field replicate and homogenized independent of the other field replicates. The four sediment bioassays used included 10 day survival and growth of *Chironomus riparius*, 28 day survival and growth of *Hyalella azteca*, 21 day survival and growth of *Hexagenia limbata* and 28 day survival and reproduction of *Tubifex tubifex*. All assays were run under static conditions in a climate controlled chamber, and no test organisms were fed. Because of confounding effects of resident fauna, primarily predation and competition, sediment was sieved through 250 μm mesh prior to testing. Results were compared

with an extensive data base from reference communities throughout the Great Lakes
(Reynoldson et al 1994).

FIGURE 2

Collingwood Harbour sample locations 1992-93



ANALYTICAL METHODS

Statistical methods:

Analyses of variance was used to examine differences among bioassay responses and bioaccumulation of contaminants by biomonitor and bioassay species using the computer software package STATGRAPHICS. In the 1992/93 east harbour and shipyard investigation, two methods were used to relate community structure and bioassay responses to environmental variables. The variables were:

Depth (m), Nitrate (mg.L^{-1}), Silt (%), Al ($\mu\text{g.g}^{-1}$), Ca ($\mu\text{g.g}^{-1}$), Loss on Ignition (%), Alkalinity (mg.l^{-1}), Na ($\mu\text{g.g}^{-1}$), and pH (aqueous).

Canonical correspondence analysis and multiple discriminant analysis were both conducted in a stepwise fashion using the computer software packages TWINSPAN, DECORANA, SYSTAT and STATISTICA. Using PCA, test sites were ordinated with reference sites, to determine whether test site community structure and bioassay responses fell within the boundary of the reference sites. The analysis predicts the responses of organisms to harbour sediment on the basis of anticipated responses that would occur in clean, reference systems, given similar values for the environmental variables listed above. If contaminants are present at sufficiently high bioavailable concentrations to cause adverse biological effects, then the predictions should fail, thereby identifying toxicity associated with the sediment.

Chemical analyses:

All chemical analyses followed the Ontario Ministry of Environment and Energy protocols detailed in "Outlines of Analytical Methods" (MOEE, 1983). Following this procedure, > 2.5 gm of organisms were digested in nitric:perchloric acid (5ml:2ml) at room temperature for several hours, at 120 °C for two hours followed by 170 °C for 4 hr. Digestion tubes were allowed to cool, sample volume brought to 25 ml with double distilled water, and analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy or by Flameless Atomic Absorption Spectrophotometry. Quality control was monitored by the inclusion of replicates and routine blanks, spikes and standard solutions. Depending upon the final test organism biomass available for analysis, duplicate or triplicate analyses were performed. Blank and standard solutions were analyzed once per run of 15 to 20 samples.

Total organic carbon was determined by measuring both total carbon and percent inorganic carbon and then subtracting to obtain total carbon. Total carbon was analyzed using the Leco CR-12 Carbon Analyzer to combust the sample at 1370 °C to remove carbonates. Carbonate carbon was measured as CO₂ evolved by reaction of carbonate with 2N HCl swept by purified air through a KI scrubber into the cathode compartment of a coulometer.

Particle size was evaluated using the standard Ontario Ministry of Environment and Energy protocol, employing a Leeds and Northrup Laser Diffractor. Samples were air

dried, disaggregated by hand with a mortar and pestle, and the >2mm size fraction discarded. Slurries containing Calgon (sodium hexametaphosphate) as a dispersant were introduced into the instrument and laser diffraction was measured. This technique provides information on particle sizes ranging from 0.17 um to 1000 um. The greater than 1000 um fraction was quantified, but not further subdivided. Comparison of this method with the pipette method demonstrates that the aggregations of fine organic particles are better dispersed and particle size distributions more accurately reflect sediment characteristics using the laser diffractor.

For PCBs and organochlorines, tissues were digested in concentrated HCl and then extracted with 25% dichloromethane in hexane (v/v). Powdered NaHCO₃ was added to the extract to neutralize the sample. The extract was dried over Na₂SO₄ and volumetrically diluted to 100 mL in hexane. Aliquots were submitted for cleanup using dry Florisil 100-200 mesh, dry pack. Extracts were analyzed by electron capture (Ni⁶³)-gas chromatography using a Hewlett Packard gas chromatograph.

Tissues for PAH analyses were digested as above, with the addition of 0.5 mL of d₁₀ anthracene following dichloromethane addition. The samples were then subjected to vortex evaporation to 1 mL and to final dryness using nitrogen. 2.5 mL of dichloromethane-cyclohexane were added to the residue, and the solutions were cleaned up using the SEHPLC system. The vortex-evaporated PAH fractions were resuspended in 0.5 mL isoctane and analyzed by a Hewlett-Packard 5790 capillary

gas chromatograph/mass selective detector with a HP ChemStation Data Station. d_{12} , chrysene was used as the internal standard.

RESULTS

Sediment bioassays

Mortality

Collingwood Harbour sediment was not lethal to mayfly nymphs (*Hexagenia limbata*) or to juvenile fathead minnows (*Pimephales promelas*). Mayfly mortality ranged from 0 to 13% and there was no apparent pattern with respect to bioassay design. No fathead minnow mortality was observed. Analysis of variance revealed that values were not significantly different from 15%, a value which current protocols have set as acceptable for reference responses to uncontaminated sediment.

Growth:

At station 21, mayflies gained more weight in the intact sediment cores than in the bulk and surficial sediment. Biomass differences were not significant at station 20 (Figure 3). In general, fathead minnows tend to lose weight in this static beaker design of the sediment bioassay since food is withheld and nutrients can only be acquired via sediment ingestion (Krantzberg 1990). Nevertheless, for station 21 fathead minnows maintained their weight in the intact sediment cores and analysis of variance (ANOVA) confirmed that significantly less weight was lost in station 20 core tube exposures compared to controls and to other treatments (Figure 4). All other treatments resulted in biomass loss that did not differ significantly from controls ($p > 0.05$).

FIGURE 3
HEXAGENIA FINAL BIOMASS
COLLINGWOOD HARBOUR BIOASSAY, 1988

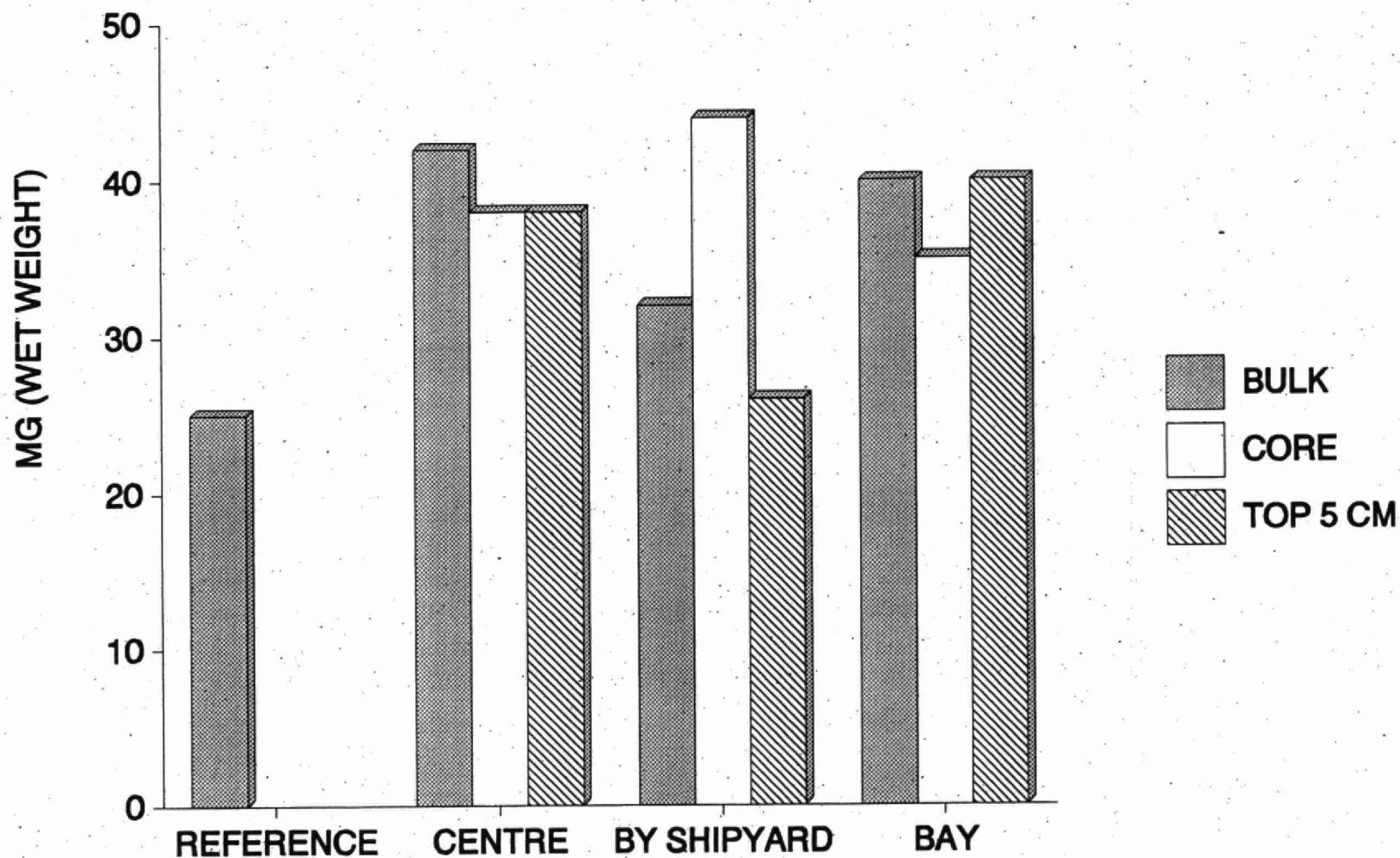
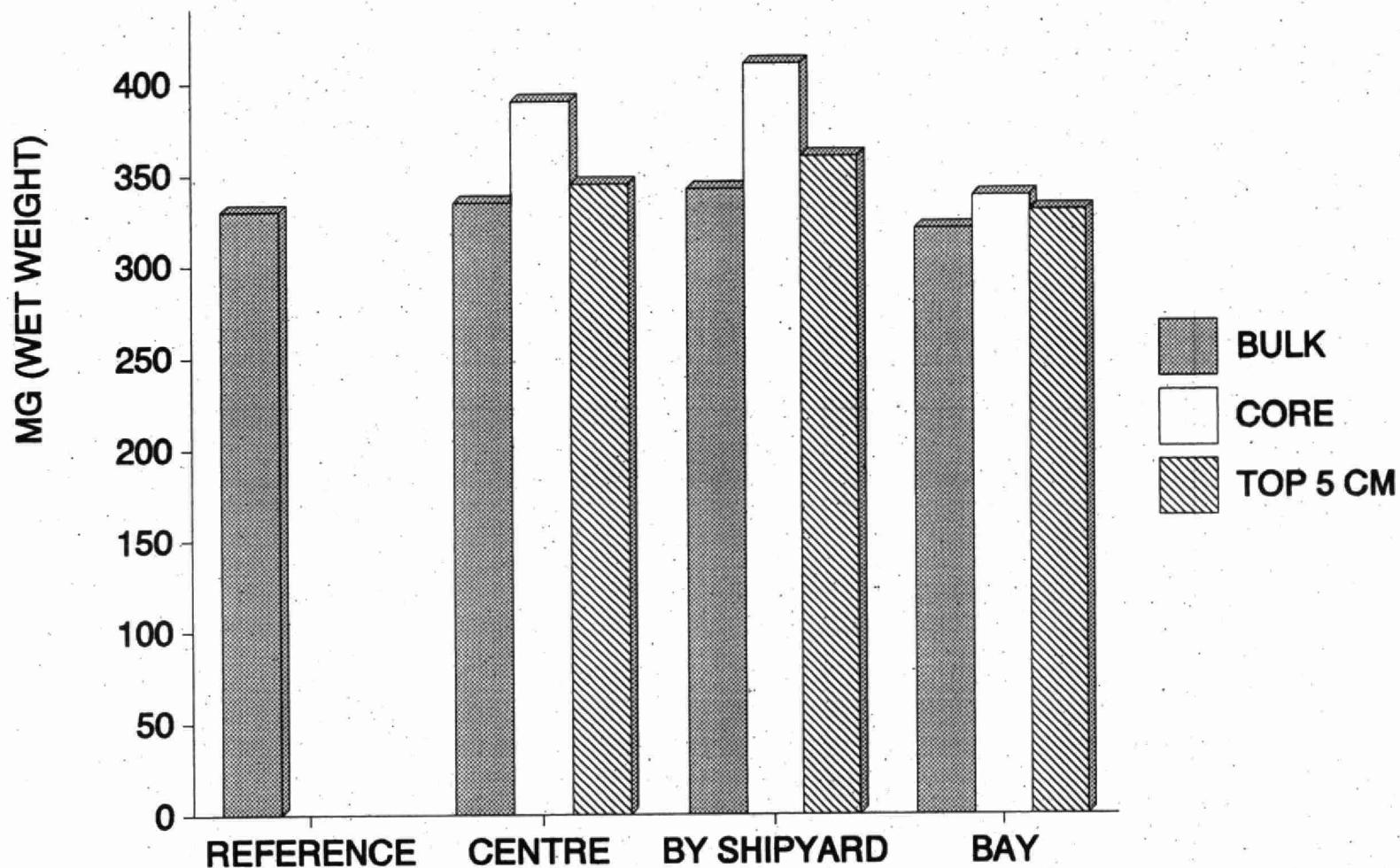


FIGURE 4

FATHEAD MINNOW FINAL BIOMASS
21 DAY BIOASSAY, COLLINGWOOD HARBOUR, 1988



Bioaccumulation

Few differences were observed in tissue concentrations of trace metals in mayflies or fathead minnows as a function of exposure to bulk, surficial, or intact sediment. PCB residues in bioassay organisms were consistently lower in intact core treatments than in the bulk and surficial sediment treatments (Table 1, 2). Lead concentrations in mayflies were variable and exceeded those of controls, however, the elevated concentrations measured in the 1986 bioassay at these stations were not reproduced. Lead concentrations of 1 to 3 $\mu\text{g.g}^{-1}$ wet weight are comparable with the resident infauna tissue residues measured in 1986 (4 - 5 $\mu\text{g.g}^{-1}$) and are lower than values which have been observed for remote shield lakes (Krantzberg and Stokes 1988). Lead concentrations of 0.5 - 3.0 $\mu\text{g.g}^{-1}$ wet weight in fathead minnows were within the range observed for sculpins collected from the harbour in 1986 (0.2 - 5.9) (Krantzberg et al 1989). Sediment chemistry is presented in Table 3.

Sediment core profiles

Bioassay stations

Lead profiles in sectioned cores from stations used in the bioassays (Figure 5) showed a pronounced augmentation of Pb concentrations with depth at station 21. In bulk sediment collected by the shipyards, Pb in minnows was significantly elevated over the concentrations in minnows exposed to intact cores (Figure 6). Copper also tended

to increase with depth. Other metal profiles were fairly stable for stations 20 and 21, and at station 21, total phosphorus and total Kjeldahl nitrogen (TKN) were at higher concentrations in surficial sediment and decreased with depth. Despite the proximity of station 21 to the Shipyards, Zn was only marginally above the MOEE lowest effect level (LEL) of 120 ug.g⁻¹.

Transect stations

The transect locations for the confined disposal facility (C1 - C5) and the Shipyards (S1 - S4) are illustrated in Figure 1. No tin was detected in sediment from cores collected in the vicinity of the Shipyard's dry docks. Lead and Zn concentrations in some of the sediment cores within 50m of the Shipyard's concrete walls approached the MOEE Severe Effect Level (SEL) of 250 and 820 ug.g⁻¹ respectively (Persaud et al. 1992) (Figure 7). No consistent depth gradients were apparent. Note that station 21 is in the vicinity of the Shipyard's property and sediment from that station revealed no adverse biological impacts as measured by growth and survival.

At some stations in the vicinity of the confined disposal facility (Table 5), total organic carbon, total phosphorus, Cr, Cu, Pb, Mn, and Zn exceeded the LEL. No spacial gradients were detected. Site specific biological testing at station 20, in proximity to the transect stations and of comparable chemistry found no effects of sediment on growth and survival.

TABLES 1 & 2

METALS AND PCBs IN BIOASSAY ORGANISMS, COLLINGWOOD HARBOUR SEDIMENT 1989, ALL VALUES IN ug/g DRY WEIGHT

TREATMENT	STATION	AI	As	Cd	Cr	Cu	Fe	Pb	Mn	Hg	Ni	Zn	PCB
FATHEAD MINNOWS													
BULK	CULTURE	378	0.86	0.068	1.26	9.9	783	0.9	25	0.48	ND	168	2.50
SURFACE	CULTURE	193	0.62	0.024	0.57	11.4	847	0.2	29	0.54	1.4	188	0.47
BULK	20	179	0.87	0.064	1.05	10.4	367	3.3	11	0.46	0.9	157	0.87
CORE	20	172	2.40	0.213	3.42	21.2	2161	16.3	58	0.44	3.9	189	1.50
SURFACE	20	347	0.80	0.128	1.36	16.7	714	2.8	21	0.48	1.5	201	0.90
BULK	21	352	0.95	0.085	1.52	11.7	725	10.2	23	0.43	1.5	156	1.15
CORE	21	922	1.80	0.213	2.47	17.5	1797	4.5	52	0.42	3.6	178	0.87
SURFACE	21	343	0.72	0.087	1.74	15.4	786	3.7	20	0.43	3.6	185	1.10
BULK	387	370	0.96	0.065	0.64	11.7	312	0.6	11	0.43	0.9	178	0.99
MAYFLY NYMPHS													
BULK	CULTURE	2933	1.58	0.72	6.58	15.6	5106	7.3	265	0.048	7.2	189	3.80
SURFACE	CULTURE	1631	0.69	0.74	3.75	13.8	2890	4.0	171	0.041	3.5	202	0.73
BULK	20	1644	1.49	0.63	4.05	22.7	3399	18.7	127	0.061	6.4	192	2.40
CORE	20	2100	1.77	0.39	5.23	29.1	3969	25.4	115	0.072	7.7	194	1.35
SURFACE	20	1513	1.78	0.69	3.94	22.3	3023	17.1	104	0.071	6.6	184	1.81
BULK	21	1533	1.59	0.58	4.37	25.1	3146	23.4	121	0.076	6.5	210	2.07
CORE	21	1897	2.08	0.41	4.00	24.6	3803	17.2	121	0.078	6.5	184	1.48
SURFACE	21	1790	2.07	0.77	4.72	26.0	3490	23.8	116	0.076	6.7	223	1.94
BULK	387	1326	2.35	0.47	2.87	17.1	2931	16.6	88	0.043	6.6	172	0.78

TABLE 3

CHEMISTRY OF SEDIMENT CORES FOR STATIONS USED IN BIOASSAYS, 1988

STATION	DEPTH	Cu	Ni	Pb	Zn	Fe	Mn	Al	Cd	Cr	Hg	TOC
20	2	32.7	17.3	43.7	86.7	14333	443	10733	0.79	21.3	0.073	18.7
	4	33.3	18.0	43.7	86.3	14000	457	10133	0.85	20.3	0.063	17.0
	6	31.3	17.3	44.0	84.7	14667	460	11333	0.91	20.3	0.110	17.3
	8	31.7	17.7	44.0	82.3	15000	463	11667	0.86	20.7	0.100	13.3
	10	29.3	17.3	43.3	79.0	14667	460	11000	0.80	19.7	0.107	18.7
	14	31.7	16.7	49.0	86.3	13667	437	10200	0.81	19.3	0.093	18.0
	18	35.0	18.0	50.0	93.0	15000	460	11000	0.86	19.0	0.110	20.0
STATION	DEPTH	Cu	Ni	Pb	Zn	Fe	Mn	Al	Cd	Cr	Hg	TOC
21	2	51.3	19.7	88.0	163.3	16000	457	11333	0.94	24.0	0.200	23.3
	4	54.7	21.3	97.0	166.7	16667	477	11667	0.96	27.3	0.160	25.3
	6	55.0	21.0	94.3	170.0	17000	477	11667	1.00	26.0	0.140	25.0
	8	50.7	21.7	82.0	163.3	17333	483	12000	1.04	26.0	0.143	25.0
	10	49.7	20.3	78.3	160.0	18333	480	12000	0.98	26.7	0.120	21.0
	14	53.7	22.0	98.7	176.7	18667	490	12667	1.10	28.7	0.127	24.0
	18	56.3	19.7	143.3	173.3	18000	470	12000	1.13	27.3	0.147	22.3

FIGURE 5

LEAD PROFILES IN SEDIMENT CORES COLLINGWOOD HARBOUR, 1988

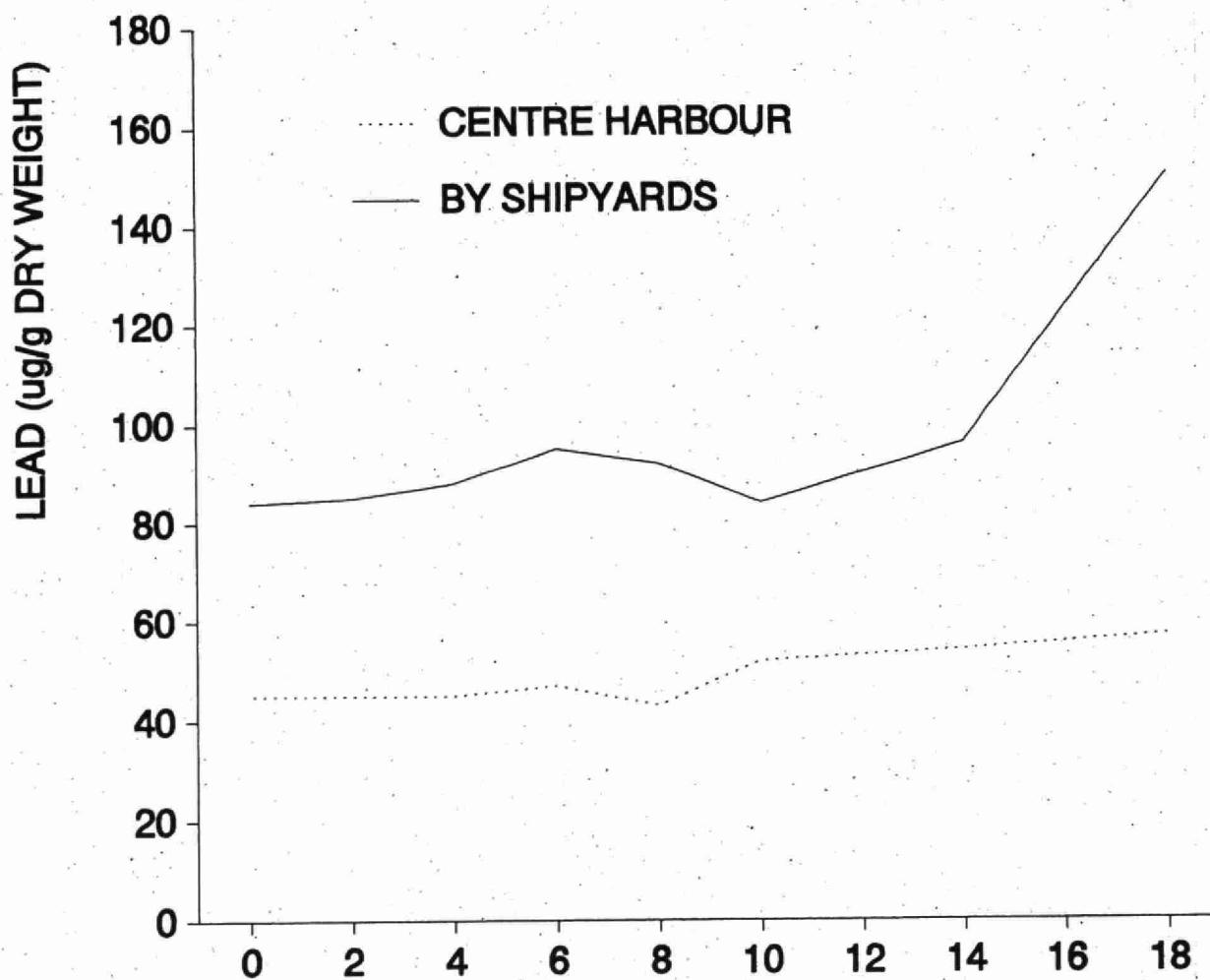
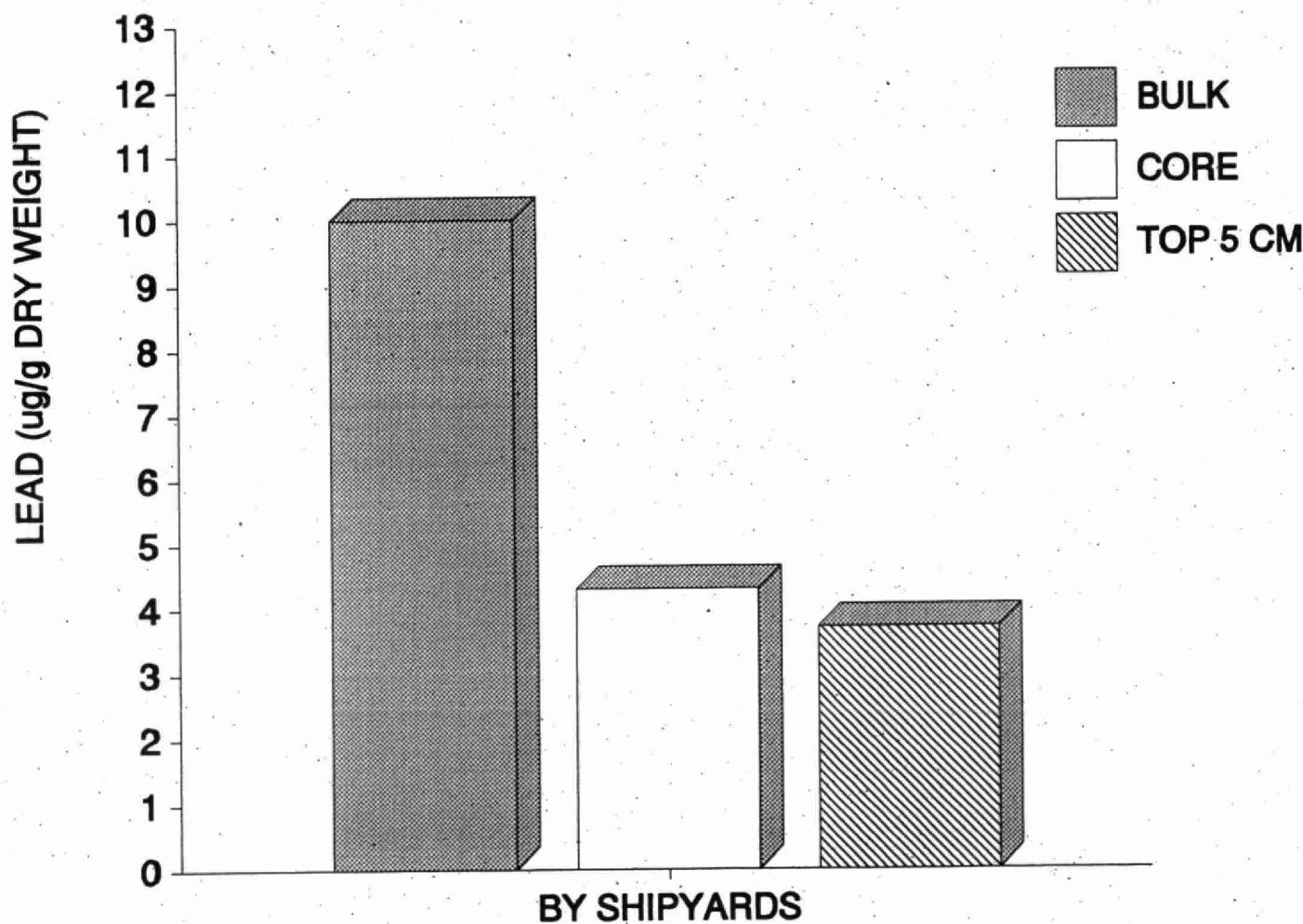


FIGURE 6

LEAD CONCENTRATION IN FATHEAD MINNOWS COLLINGWOOD HARBOUR BIOASSAYS, 1988



Mussel Biomonitoring

The results of mussel and sediment collections and analyses are described by station.

The full data sets are found in Tables 5 - 7.

OAK STREET CANAL (14) elevated zinc in mussels, very low concentrations of all other metals in mussels and sediment. No detectable pesticides in mussels and sediment, traces of some PAH in sediment.

HICKORY STREET CANAL (15) elevated zinc in sediment, very low concentrations of all other metals; organic contaminants in sediment at detection limit and below detection in mussels.

BLACK ASH CREEK (13) low concentrations of all metals in sediment and mussels; no detectable organic contaminants in sediment and mussels.

GOODYEAR OUTFALL (11) elevated zinc in sediment and mussels, low concentrations of all other metals and no detectable organic contaminants in sediment and mussels.

CENTRE HARBOUR (25) low concentrations of all metals in sediment and mussels; no detectable organic contaminants in sediment and mussels.

EAST HARBOUR BY SHIPYARDS (21) low concentrations of all metals in sediment and mussels; organic contaminants in sediment at detection limit and below detection in mussels

STP PRECHLORINATION (3) low concentrations of all metals in sediment and mussels; no detectable organic contaminants in sediment and mussels.

WEST HARBOUR DEFUNCT IMPERIAL OIL WHARF, BLACK ASH CREEK MOUTH (32)
low concentrations of all metals in sediment and mussels; no detectable organic contaminants in sediment and mussels

Table 6

TRACE METALS IN MUSSEL BIOMONITORS PLACED IN COLLINGWOOD HARBOUR AND HARBOUR TRIBUTARIES FOR THREE WEEKS, 1990. ALL VALUES ARE $\mu\text{g.g}^{-1}$ (PARTS PER MILLION) ON A WET WEIGHT BASIS, FOR MUSSEL TISSUE, EXCLUSIVE OF THE SHELL.

STATION DESCRIPTION		DESCRIPTION	Cu	Ni	Pb	As	Cd	Se	Hg	Zn	Mn
C	BALSAM LAKE CONROL		1.35	0.50	0.80	0.74	0.54	2.14	0.01	31.5	1280
13	BLACK ASH CREEK		1.17	0.50	0.70	0.62	0.51	0.60	0.01	36.3	780
14	OAK ST. CANAL		1.73	0.43	0.63	0.77	0.58	0.77	0.01	63.0	940
15	HICKORY ST. CANAL		3.77	0.43	0.63	0.58	0.43	0.90	0.01	39.3	713
11	GOODYEAR		2.87	0.47	0.79	0.44	0.71	0.78	0.01	41.3	1503
3	STP ¹ PRECHLORINATION		0.86	0.47	0.67	0.48	0.82	0.81	0.02	31.7	456
21	EAST HARBOUR		1.06	0.47	0.67	0.44	0.41	0.96	0.01	32.7	506
25	CENTRE HARBOUR		1.01	0.43	0.63	0.61	0.56	1.10	0.01	40.0	546
32	BLACK ASH CREEK MOUTH		1.33	0.47	0.67	0.74	0.83	0.90	0.02	49.7	1546

¹sewage treatment plant, prechlorination

TABLE 7 POLYAROMATIC HYDROCARBONS² DETECTED IN SEDIMENT FROM COLLINGWOOD HARBOUR AND THE TRIBUTARIES WITHIN THE HARBOUR WATERSHED, 1990. VALUES ARE IN $\mu\text{g.g}^{-1}$ (parts per million) DRY WEIGHT. NO SEDIMENT WAS COLLECTED FROM THE STP PRECHLORINATION CHAMBER.

COMPOUND	DETECTION LIMIT	STATION 11 GOODYEAR OUTFALL	STATION 13 BLACK ASH CREEK	STATION 14 OAK STREET CANAL	STATION 15 HICKORY STREET CANAL	STATION 21 EAST HARBOUR	STATION 25 CENTRE HARBOUR	STATION 32 MOUTH OF BLACK ASH CREEK
ANTHRACENE	0.01	<0.01	<0.01	0.16	<0.04	<0.02	<0.01	<0.01
FLUORANTHENE	0.02	<0.02	<0.02	<0.02	0.76	0.23	<0.02	<0.02
PYRENE	0.02	<0.54	<0.06	1.40	0.80	<0.20	<0.06	<0.06
BENZO (a) ANTHRACENE	0.02	<0.02	<0.02	0.53	<0.04	<0.07	<0.02	<0.02
CHRYSENE	0.02	<0.05	<0.02	0.62	0.44	<0.10	<0.02	<0.02
BENZO (k) FLUORANTHENE	0.02	<0.02	<0.02	0.27	0.22	<0.11	<0.06	<0.06
BENZO (a) PYRENE	0.04	<0.04	<0.04	<0.38	<0.24	<0.08	<0.04	<0.04
INDENO (1,2,3-cd) PYRENE	0.04	<0.04	<0.04	<0.19	<0.26	<0.05	<0.04	<0.04

² sediment was analyzed for over 40 additional trace organic compounds including other PAHs, organochlorine pesticides, PCBs and mirex. All values were below detection limits.

Table 7 TRACEMETALS IN SEDIMENT FROM COLLINGWOOD HARBOUR AND HARBOUR TRIBUTARIES FOR THREE WEEKS, 1990. ALL VALUES ARE $\mu\text{g.g}^{-1}$ (PARTS PER MILLION) ON A DRY WEIGHT BASIS

STATION DESCRIPTION		TOC ³	Cu	Ni	Pb	As	Cd	Se	Hg	Zn	Mn
13	BLACKASH CREEK	0.2	9.5	12.0	1.6	0.99	0.05	0.20	0.02	30	220
14	OAK ST. CANAL	1.1	15.0	12.0	32.0	1.7	0.30	0.20	0.05	120	220
15	HICKORY ST. CANAL	5.0	50.0	27.0	160.0	5.4	0.68	0.67	0.13	600	350
21	EAST HARBOUR	2.7	46.0	28.0	51.0	3.4	0.77	0.46	0.12	130	490
25	CENTRE HARBOUR	0.5	12.0	15.0	4.9	1.7	0.05	0.20	0.02	27	270
32	BLACKASH CREEK MOUTH	0.5	5.8	8.4	3.1	0.48	0.05	0.20	0.02	25	170
SEDIMENT GUIDELINES(LEL) ⁴		1.0	16	16	31	6	0.6	-	0.2	120	460

³total organic carbon, expressed as percent

⁴LEL: lowest effect level, to replace the open water disposal guidelines

1991 Benthic Community Structure

A maximum of 28 species was found at a given station in Collingwood Harbour and the inflows. Species composition was typified by an oligochaete-chironomid assemblage. Naid and tubificid oligochaetes were ubiquitous, as were the chironomini. Amphipods, gastropods, sphaerids and insect species included pollution intolerant representatives such as *Pontoporia*, *Cragonyx*, *Pisidium*, *Sphaerium*, and *Ephemeroptera* (Table 8).

TABLE 8. BENTHIC MACROINVERTEBRATE COMMUNITY STRUCTURE, COLLINGWOOD HARBOUR 1991

Benthic Invertebrates Collingwood Harbour 1991

STATION	13	14	15	11	21	22	27	28	34	62
COELENTERATA										
<i>Hydra sp.</i>	2	-	-	-	-	-	-	-	-	-
COLLEMBOLA	-	-	1	-	-	-	-	1	-	-
NEMATODA	1	2	-	388	11	1	-	-	5	-
PLATYHELMINTHES										
TURBELLARIA	1	-	-	-	8	1	-	-	1	-
ANNEIIDA: OLIGOCHAETA										
NAIDIDAE										
<i>Dero nivosa</i>	3	-	-	-	-	-	-	-	-	-
<i>Dero furcata</i>	20	-	-	178	-	-	-	-	-	-
<i>Naia bretschneri</i>	185	1	-	-	-	-	1	1	2	-
<i>Naia elongata</i>	-	-	-	-	-	3	-	1	2	-
<i>Naia simplex</i>	8	-	-	-	-	-	1	-	20	18
<i>Naia variegata</i>	37	2	-	-	-	-	2	1	33	20
<i>Ophidona serpentina</i>	-	-	-	-	-	-	-	-	85	-
<i>Slevina appendiculata</i>	4	-	-	-	-	-	-	-	-	-
<i>Specaria jasinea</i>	-	-	-	-	-	-	-	1	-	-
<i>Styliaria lacustris</i>	-	-	-	-	-	-	-	-	1	-
<i>Uncinella uncinata</i>	-	-	-	-	-	-	-	1	-	-
TUBIFICIDAE										
<i>Aulodrilus limnophilus</i>	1	-	-	-	-	-	-	-	-	-
<i>Aulodrilus piqueti</i>	-	-	-	-	-	10	-	-	-	2
<i>Ilyodrilus templetoni</i>	3	2	8	-	36	34	1	5	4	5
<i>Isochaetides freyi</i>	-	1	-	-	-	-	1	2	4	-
<i>Limnodrilus cervix</i>	-	1	-	-	11	30	-	1	2	-
<i>Limnodrilus claparedianus</i>	-	-	1	-	18	6	-	1	1	-
<i>Limnodrilus hoffmeisteri</i>	3	10	48	-	128	103	1	5	9	34
<i>Limnodrilus udekemianus</i>	-	-	2	-	-	1	4	-	1	-
<i>Potamothrix vejvodovskyi</i>	-	-	-	-	-	1	1	1	8	-
<i>Quistradriplus multisetaosus</i>	-	-	-	-	8	-	-	1	1	-
<i>Spirospurina ferox</i>	-	-	-	-	448	-	7	4	17	22
<i>Tubifex ignotus</i>	-	-	-	-	-	-	1	-	1	-
<i>Tubifex tubifex</i>	-	-	4	1237	5	3	-	-	-	8
immature with chaetae	11	2	3	853	11	9	1	1	1	25
immature without chaetae	6	13	33	-	448	160	2	29	32	160
ANNEIIDA: HIRUDINAE										
<i>Helobdella stagnalis</i>	6	22	3	-	-	-	-	-	-	-
<i>Mooreobdella spp.</i>	2	-	3	-	-	-	-	-	-	-

ODONATA: Libellulidae	-	-	-	11	-	-	-	-	-	-
HEMIPTERA: Corixidae sp.	14	-	-	-	-	-	-	-	-	-
TRICHOPTERA										
<i>Helicopsyche</i> sp.	7	-	-	-	-	-	-	-	-	-
<i>Agraylea</i> sp.	-	-	-	-	6	2	-	-	-	-
<i>Hydroptila</i> sp.	6	-	-	-	-	-	-	-	-	-
<i>Oecetis</i> sp.	-	-	-	-	-	-	-	-	1	-
DIPTERA: Ceratopogonidae										
<i>Bezzia</i> sp.	2	-	-	-	-	-	-	-	-	-
<i>Probezzia</i> sp.	-	-	-	3	-	2	1	1	1	-
DIPTERA: Chironominae										
<i>Chironomid pupae</i>	7	-	-	-	-	8	1	2	8	-
<i>Chironomus</i>	93	1	-	-	19	45	1	1	-	18
<i>Cladopelma</i>	-	-	-	-	47	64	-	1	2	-
<i>Cleidotanytarsus</i>	-	-	-	-	-	-	1	3	4	-
<i>Cryptochironomus</i>	-	-	-	-	2	-	2	6	5	-
<i>Dicrotendipes</i>	4	-	-	-	-	-	-	1	4	-
<i>Endochironomus</i>	-	-	-	-	-	-	-	8	10	-
<i>Parechironomus</i>	--	-	-	-	-	-	-	-	1	-
<i>Paracladopelma</i>	-	-	-	-	-	-	-	-	1	-
<i>Paraluterborniella</i>	-	-	-	-	-	-	1	1	2	-
<i>Peratanytarsus</i>	-	-	-	-	-	-	-	-	-	-
<i>Peratendipes</i>	2	-	-	-	-	-	-	-	-	-
<i>Phaenopsectra</i>	1	-	-	-	2	-	1	-	2	-
<i>Polypedilum</i>	-	-	-	-	-	-	2	10	3	-
<i>Stempellina</i>	-	-	-	-	-	-	-	1	-	-
<i>Stictochironomus</i>	4	-	-	-	-	-	-	6	2	-
<i>Tanytarsus</i>	1	-	-	-	-	-	-	1	2	-

FIGURE 8

METALS IN SHIPYARD SLIPS (ug/g)

COLLINGWOOD HARBOUR 1992/92

Pb and Cu

10000

1000

Pb →

Cu →

100

E06

E07

E08

W09

W10

W11

Zn

100000

10000

1000

Zn SEL

100

LEAD
COPPER
ZINC

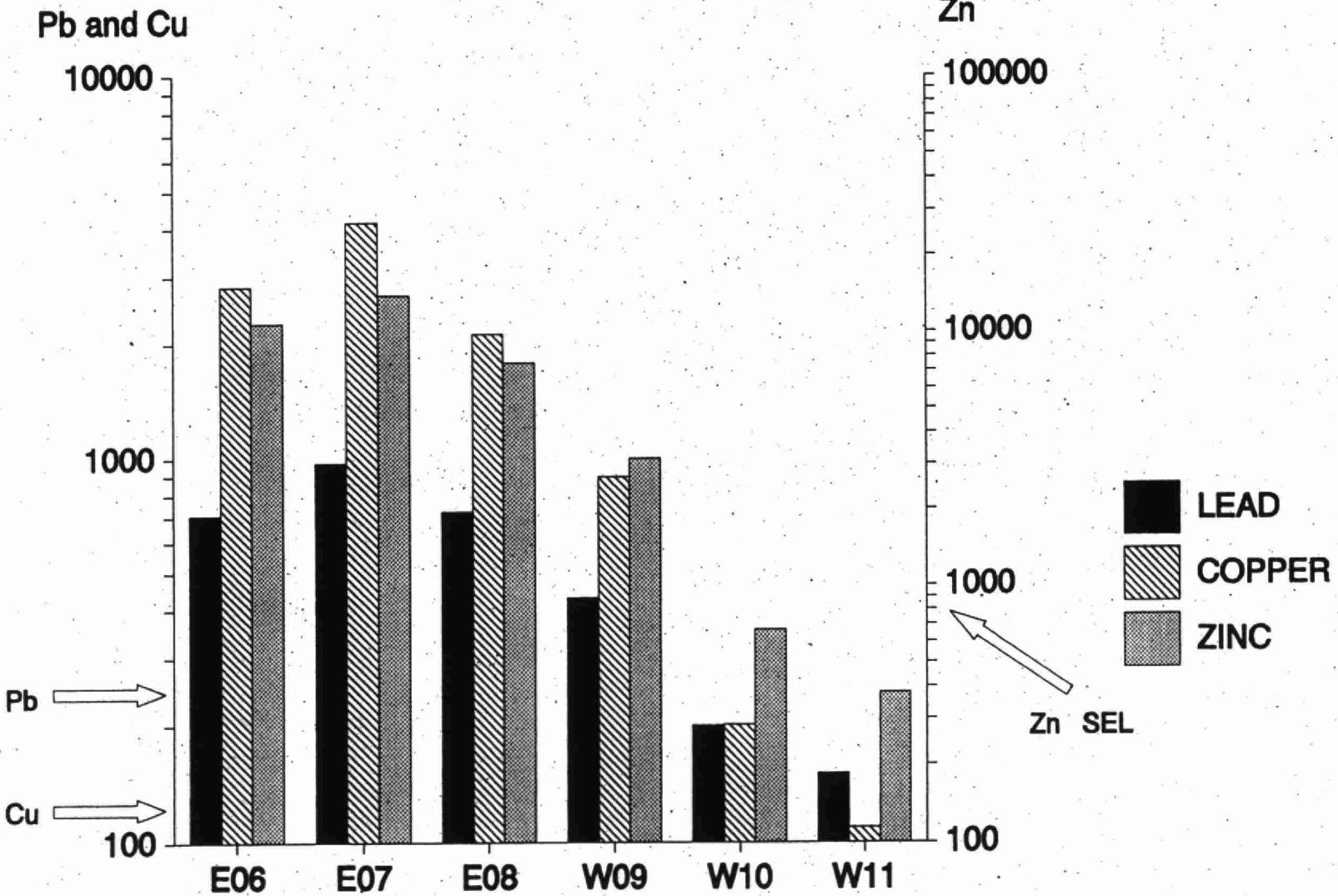


FIGURE 9

METALS OUTSIDE THE SHIPYARD SLIPS COLLINGWOOD HARBOUR 1993, NE TO SW

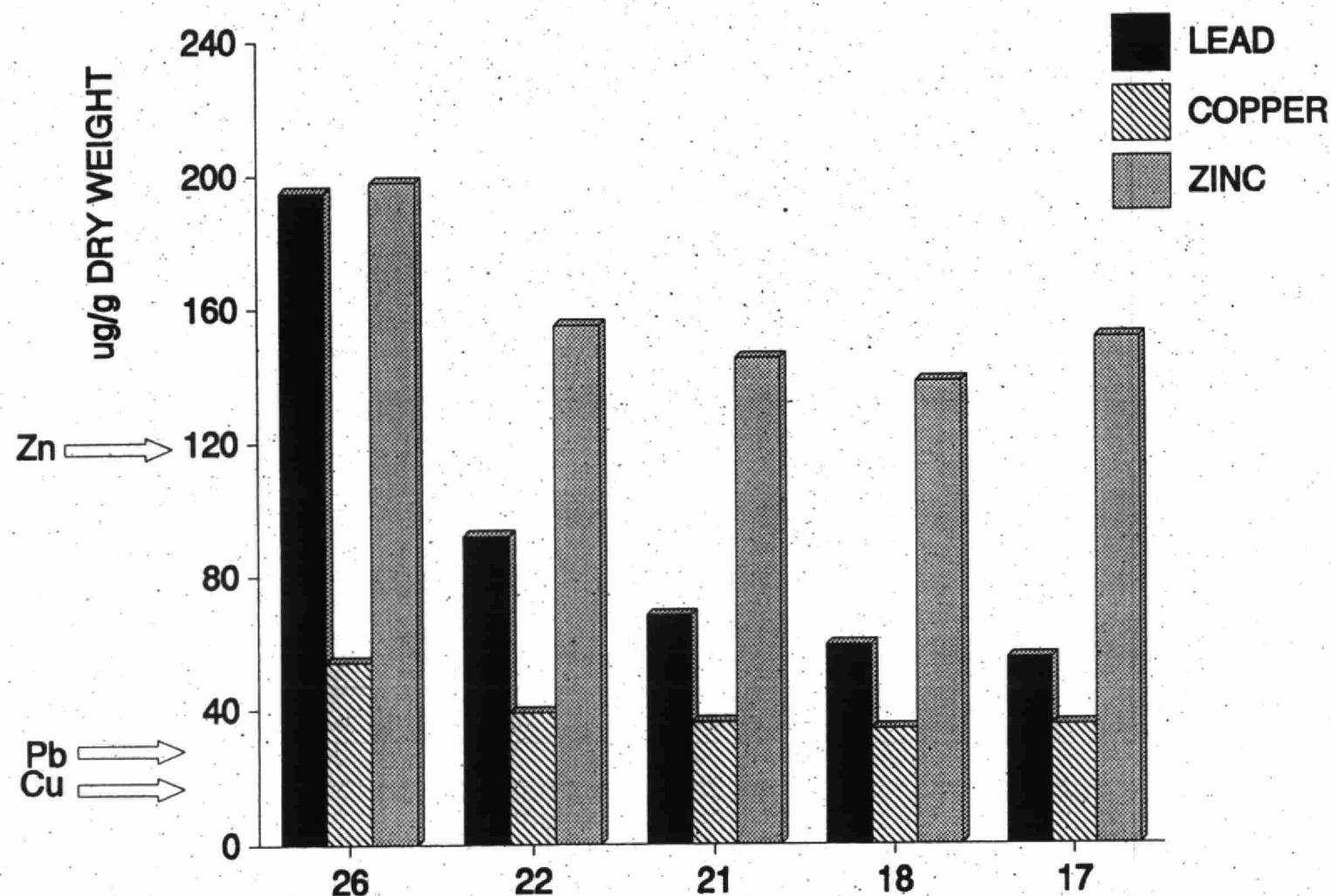
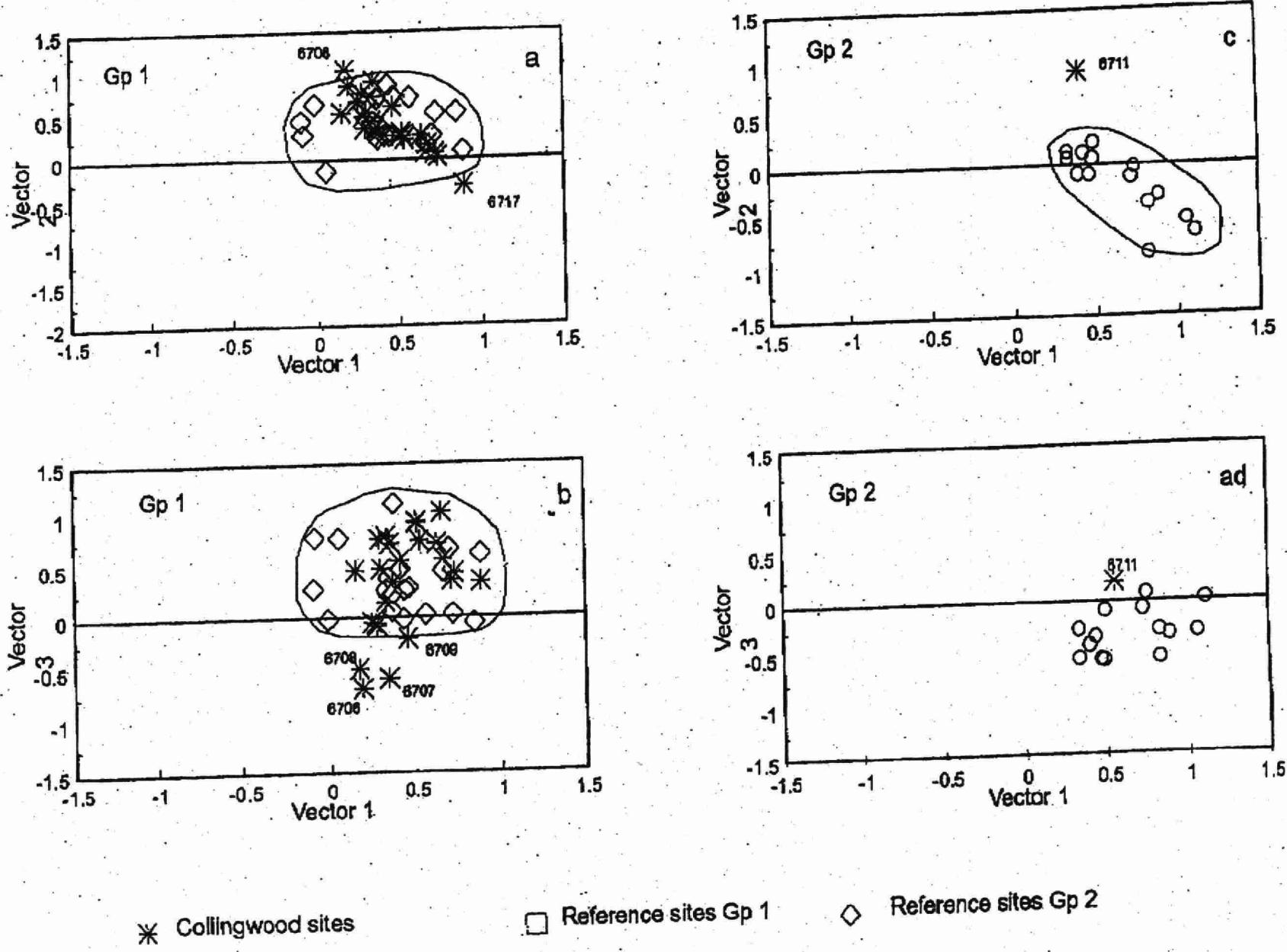


FIGURE 10: COMMUNITY STRUCTURE ANALYSIS

Comparison of Reference & Collingwood H. Sites



a community represented by group 4. This site was outside the range observed in the reference sites on vector 2.

Again using the environmental data, site grouping for the toxicity responses and sites were classified as being members of either group 1 or 2. Figures 11 and 12 indicate no adverse effects of sediment on bioassay species. Only the reproductive endpoints of cocoon production and total young for *T. tubifex* were outside the expected range, indicating chronic toxicity (Figure 13). When plotted in ordination space (Fig. 14), the sites predicted in group 1 all fell within the boundary of the reference sites. However, a number of sites predicted as group 2 fell outside the reference site boundary on vector 2 or 3. These are the same sites that had reduced *T. tubifex* young production relative to expected.

FIGURE 11

SEDIMENT BIOASSAY RESULTS 1993 SURVIVAL OF TEST ORGANISMS

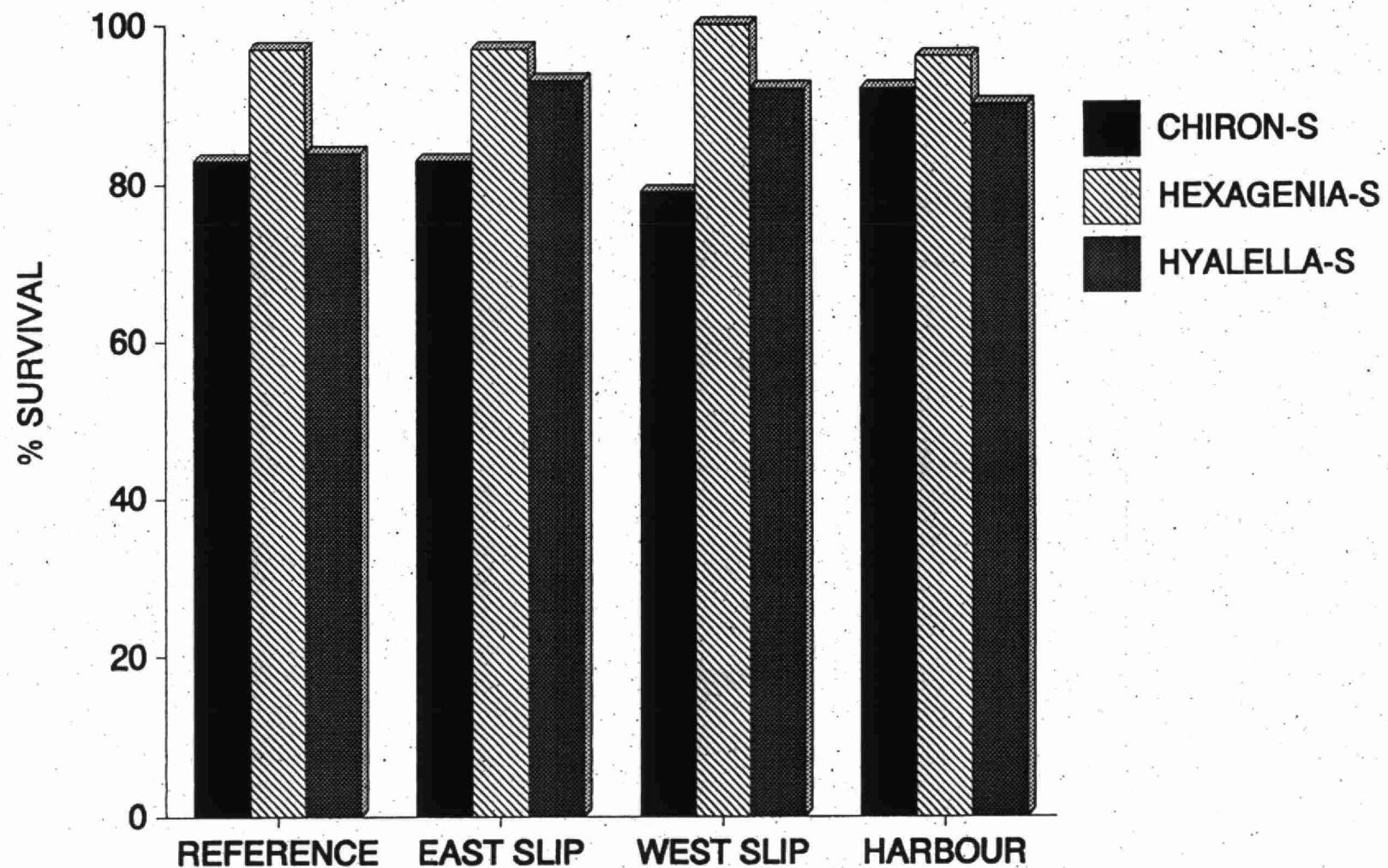


FIGURE 12

SEDIMENT BIOASSAY RESULTS 1993 GROWTH OF TEST ORGANISMS

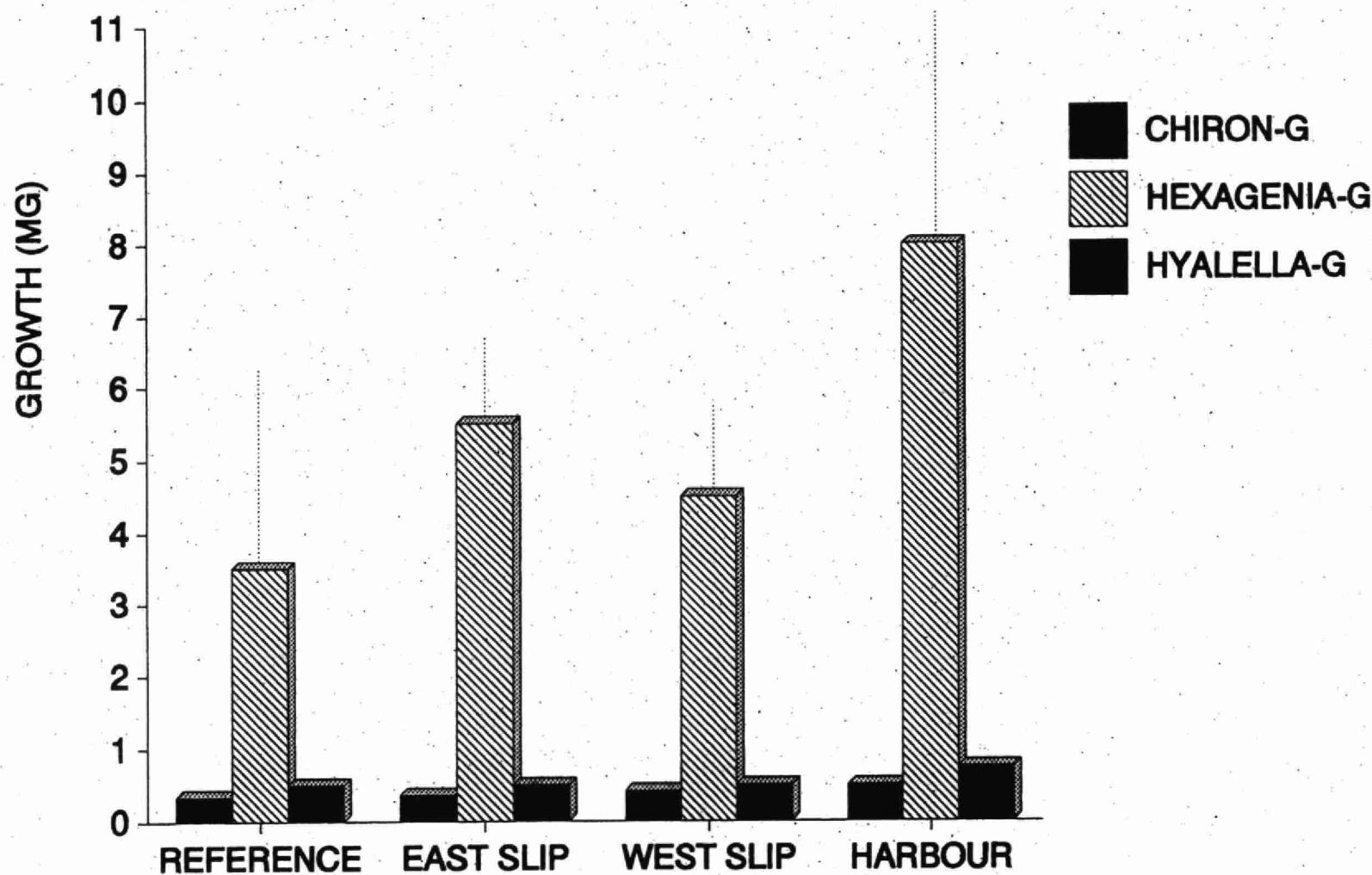


FIGURE 13

SEDIMENT BIOASSAY RESULTS 1993 NUMBER OF COCCOONS/YOUNG

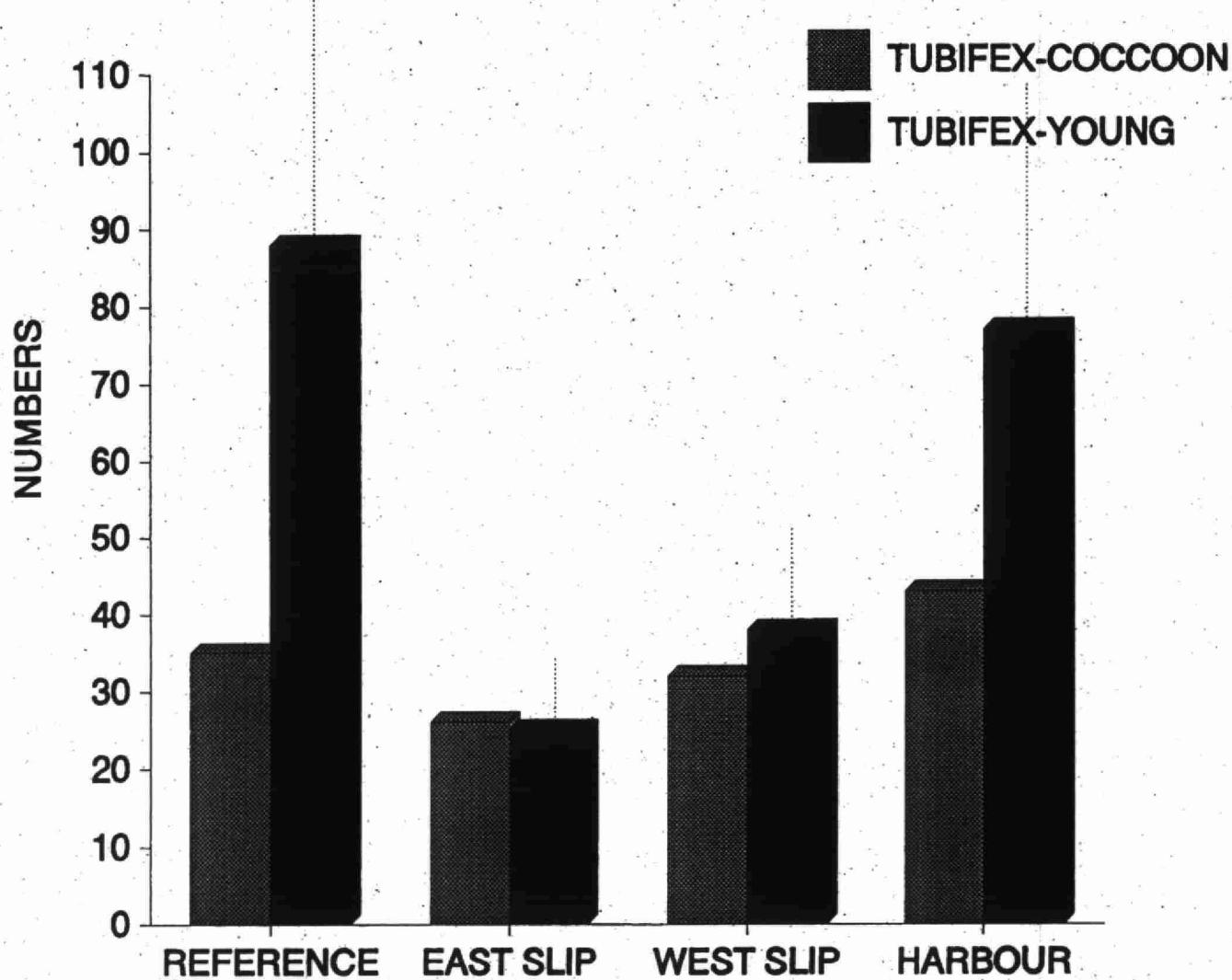
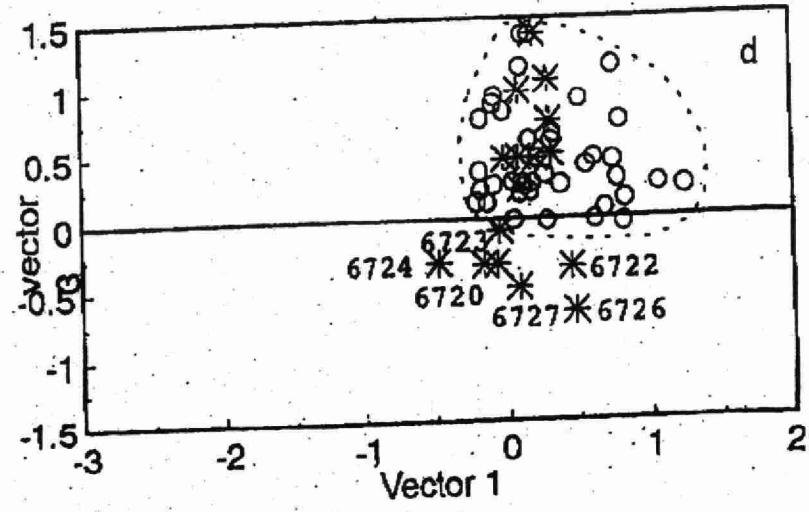
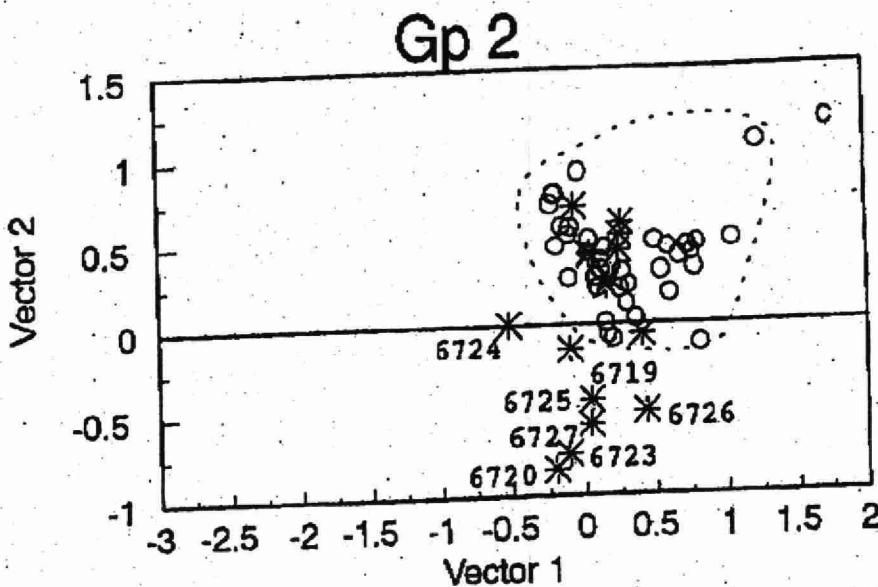
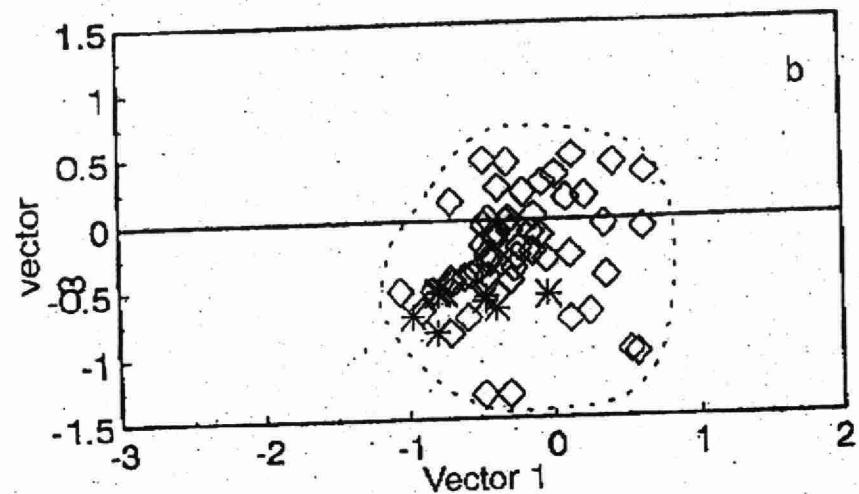
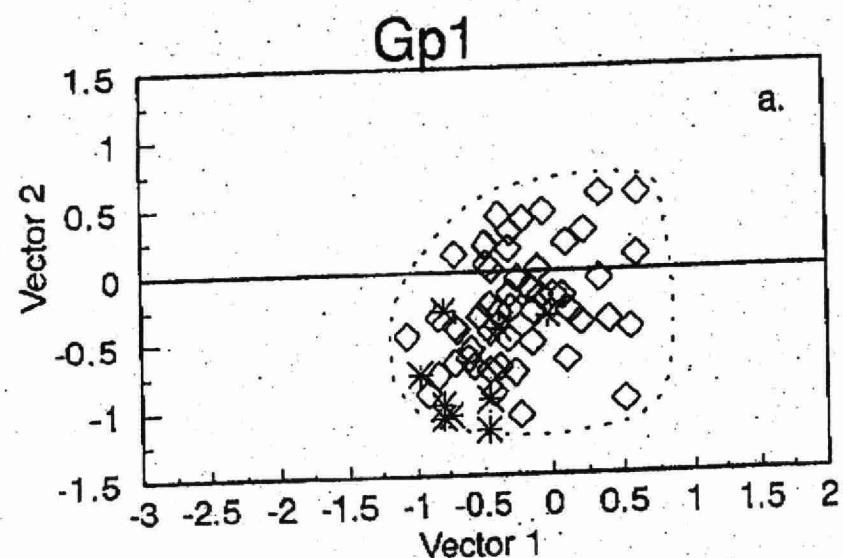


FIGURE 14: BIOASSAY RESPONSE ANALYSIS

Comparison of reference and Collingwood H. Sites (Toxicity)



Gp 1 Gp 2 Col H.

◇ ○ *

DISCUSSION

In 1985 the Great Lakes Water Quality Board recommended that Canada and the United States prepare and detailed Remedial Action Plans (RAPs) for the restoration of environmental quality and beneficial uses of 42 (now 43) identified "Areas of Concern" on the Great Lakes system. Collingwood Harbour is one of the 17 Canadian "Areas of Concern". Sediment sampling in Collingwood Harbour confirmed that areas existed where metals in sediment exceeded the LEL. Therefore, the biological availability of sediment containants was exmined to evaluate the need for and nature of seidment remediation.

Contaminants in sediment tend to associate mainly with clay/silt particles typically found in depositiona zones. This fraction includes substances active in pollutant enrichment such has hydroxides, sulfides, and amorphous and fine grained organic matter (Forstner 1987, Forstner and Wittman 1980). The first phase of the sediment assessment program was to determine whether metal and trace organic contaminants were present at concentrations sufficient to warrent further biological evaluation. Surveys conducted in 1988 and 1989 focussed on sampling the fine grained materials to determine whether contaminants were present at concentrations sufficient to impair components of the ecosystem.

The Ontario Ministry of Environment and Energy guidelines for the management of contaminated sediment (Persaud et al. 1992) has developed biologically based

chemical guidelines for metals and trace organic contaminants. The Lowest Effect Level (LEL) is the level of sediment contamination that can be tolerated by 95% of benthic organisms, while the Severe Effect Level (SEL) indicates the level at which pronounced disturbance of the benthic macroinvertebrate community can be expected. Because the LEL is based on bulk sediment chemistry and is a general guideline for the Great Lakes Basin, Persaud et al. recommend that biological tests be performed on sediment when contaminants exceed the LEL.

The sediment bioassays conducted in this study provide information on whether exceeding the LEL for some parameters is of toxicological significance. The most sensitive endpoints in the Collingwood Harbour bioassays were the growth responses and reproductive capabilities of test organisms. Growth inhibition bioassays have been used as sensitive indicators of nonlethal toxicity in chronic bioassays (Nebeker et al. 1984, Powlesland and George 1986, Brungs et al 1976, Krantzberg 1990). An absence of growth inhibition is one line of evidence that indicates sediment is not eliciting toxicity.

In the 1988 bioassay study, mayflies and fathead minnows exposed to Collingwood Harbour sediment grew as well as or better than control organisms. In particular, the intact core bioassays resulted in improved growth for fathead minnows. The same was true for mayflies at station 21. This improvement may be related to the chemical profiles observed in station 21 sediment. Deeper sediment had higher concentrations

of Pb than surficial sediment. Exposure to intact surface sediment may have improved growth due to exposure to lower concentrations of contaminants.

The 1990 mussel biomonitoring and analysis of native benthic invertebrates support the laboratory findings on toxicity and bioaccumulation. With the exception of zinc in two of the tributaries, no metal or trace organic contamination was found in exposed mussels or sediment in the creek, canals or harbour. Other than Zn and Pb, metals were below the provincial sediment guideline or at locations where concentrations were above the guidelines, values were comparable to background concentrations for the area (Krantzberg 1991b).

Zinc is an essential element and not highly toxic, except at extremely elevated concentrations. For example, Krantzberg and Boyd (1992) demonstrated no mortality, and growth comparable to controls, when mayfly nymphs and fathead minnows were exposed to sediment from Hamilton Harbour containing in excess of 2000 ug.g⁻¹. Many organisms, including freshwater mussels, are known to be capable of regulating their tissue concentration of Zn (Langston and Zhou 1986, Phillips 1985, Chu et al. 1990, Krantzberg and Stokes 1989). The poor relationship found between Zn in mussels and sediment (Figure 2) suggests that:

- a) mussels are able to modify their tissue concentrations of zinc through metabolic pathways

- b) the biological availability of zinc varies widely among stations and bulk sediment chemistry is a poor indicator of zinc that is available for uptake and retention by mussels

The land adjacent to the tributaries at the southern end of the harbour perimeter is a filled landfill site. Among the sources of waste in the landfill are Goodyear Rubber, Harding Carpets and LOF Glass (P. Dunbar, pers. comm.) It is possible that zinc in the tributaries is associated with zinc stearate used in processing rubber, which has migrated out of the landfill site. Elevated concentrations of zinc, however, are not found within the harbour and zinc is marginally elevated only in mussels in several of the inflows. In addition, due to the intermittent nature of flow in the tributaries, these streams provide poor habitat for benthos (Krantzberg, per. obs.) and fish (A. Smith, MNR, pers. comm.). The presence of emergent vegetation may also be assisting in sequestering metals from available environmental compartments. Exposure of biota to contaminants is limited by the intermittent nature of these small storm sewers.

Despite the presence of lead above the LEL and background values, for sediment from Hickory Street Canal, tissue residues in mussels are comparable to controls. The ability of mussels to accumulate metals rapidly has been shown (Lakshmanan and Nambisan 1989), nevertheless, no excessive bioaccumulation was observed. Again, this canal flows intermittently, and lead concentrations are at or below the detection

limit during high flow conditions associated with storm events (Krantzberg 1994 in prep.).

Data from the present study support previous findings that trace organic contaminants, including PAHs, are not an environmental concern for Collingwood Harbour. No PAHs, PCBs or pesticides were detected in mussels or sediment, with the exception of low concentrations of some PAHs in sediment from Oak St. Canal. Substances such as pyrene and chrysene were found, and are commonly generated as a result of incomplete combustion of fossil fuels (USEPA, 1977). The Provincial Sediment Management Guidelines (Persaud et al. 1992) have proposed that the tentative "Lowest Effects Level" (LEL) for total PAHs be $2 \mu\text{g.g}^{-1}$ dry weight. The LEL corresponds to the guideline value for the open water disposal of dredged sediment. Alden and Butt (1987) found no effects on mortality and respiration rate for grass shrimp exposed to sediment containing total PAH concentrations of 2.9 to $15.5 \mu\text{g.g}^{-1}$ and considered these materials suitable for open water disposal. Draft PAH goals for the Netherlands cite a standard value of $0.5 \mu\text{g.g}^{-1}$ for each individual PAH, which is equivalent to $8 \mu\text{g.g}^{-1}$ total PAH for the 16 compounds MOEE measures (van Veen and Stortelder, 1988). Using four separate approaches to developing sediment quality criteria, Chapman et al. (1987) derived values for PAHs at, or below which, biological effects have been shown to be minimal for PAHs. These ranged from 2.0 to $12.0 \mu\text{g.g}^{-1}$. Concentrations in Oak Street Canal sediment are in the range of these guidelines and observations, and represent concentrations typical of relatively

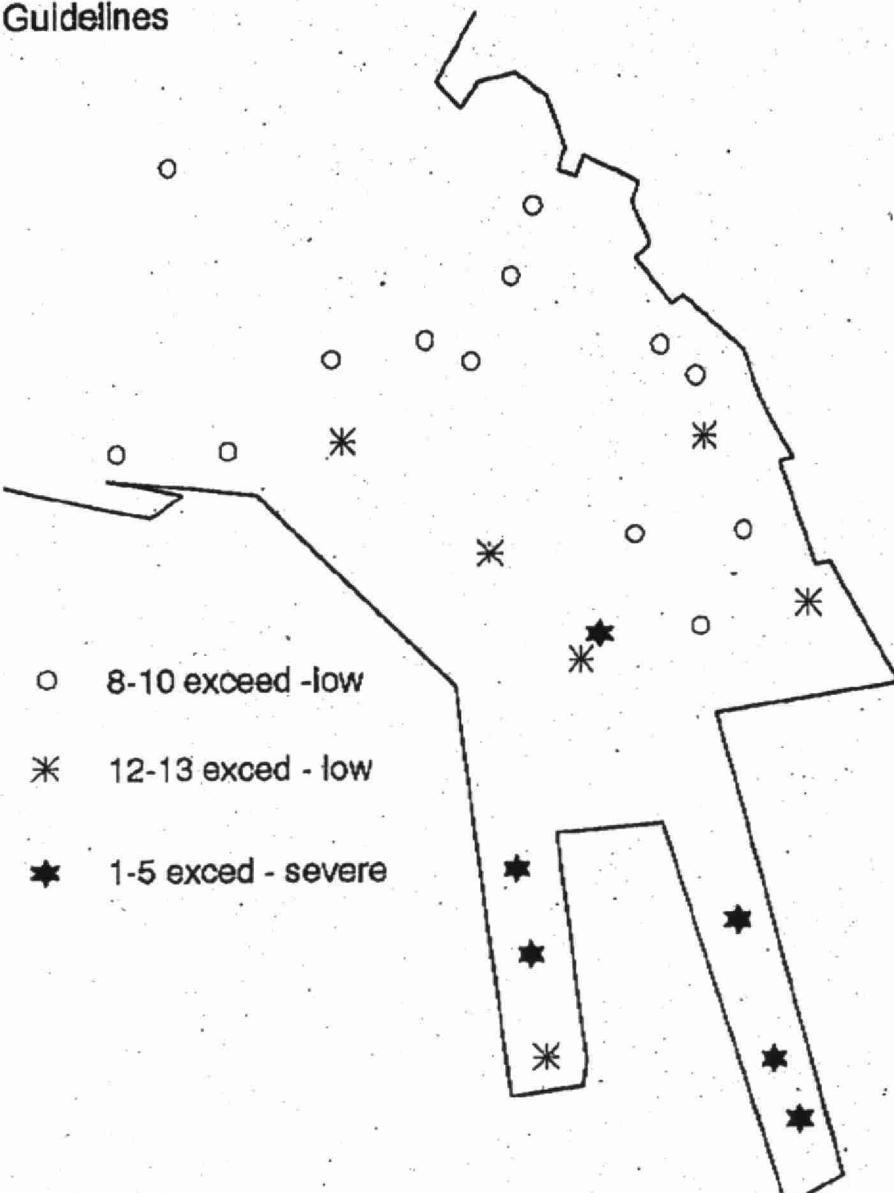
uncontaminated sites in urban watersheds. In a concurrent study, Suns also reported PAHs in young of the year spottail shiners collected from Collingwood Harbour in 1990 to be typical of regional values (Suns pers.comm.).

The sediment collected along transects at the CDF was of a chemical nature comparable to sediment at station 20. Sediment at the Shipyard's property has Zn and Pb at concentrations that approach or exceed the MOEE SEL. Metal concentrations in the sediment at station 21, approximately 100 m from the Shipyards are substantially lower than those within 50 m suggesting that the material is being contained at the Shipyard. Sediment at station 21 does not exert observable toxicity. Nevertheless, the sediment within the Shipyards property could pose a threat to the Harbour ecosystem, based on the 1992/93 evaluation.

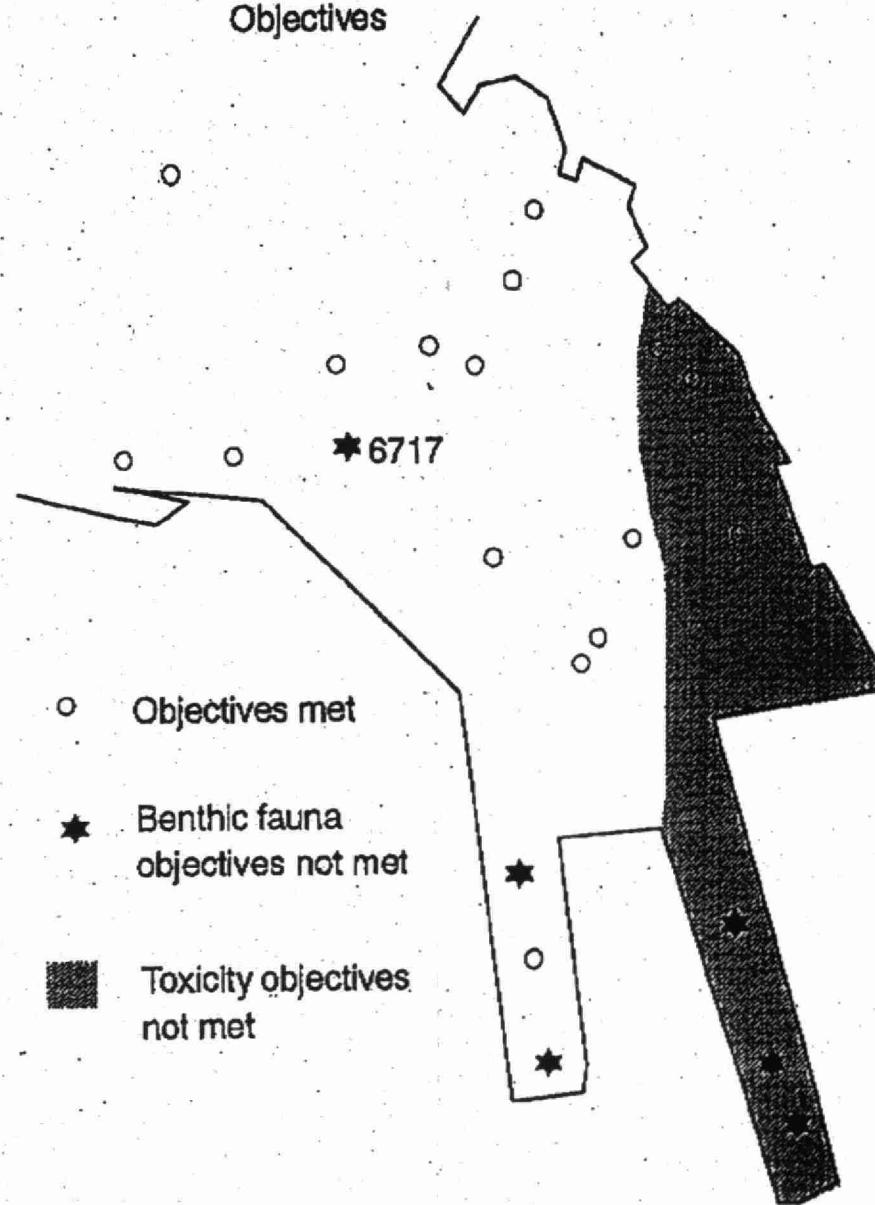
Chronic low level toxicity problems were found within the Shipyard slips and in a limited zone northwest of the slips (Figure 15). While depressed, reproduction did continue to occur in bioassay exposures, and based on the community structure, oligochaetes are abundant at those sites in the harbour that elicited low level toxicity. Part of the reduction in reproduction could be attributed to the higher clay content of these sites, which is not a preferred substrates for oligochaetes because burrowing activity is more difficult and less food is available. However, tubificids have been found to be particularly sensitive to metal contamination (Reynoldson, per. comm.), and a remedial strategy has been proposed.

FIGURE 15. APPLICATION OF BIOLOGICAL AND CHEMICAL GUIDELINES TO DETERMINATION OF ZONES OF SEDIMENT REMEDIATION. COLLINGWOOD HARBOUR, EAST. 1993.

**Chemical
Guidelines**



**Biological
Objectives**



RECOMMENDED STRATEGY FOR RESTORATION OF SEDIMENT QUALITY:

- Given that mussels in the harbour did not have elevated tissue residues relative to controls, the zinc elevations in the intermittent storm sewers do not warrant extensive and highly costly remediation of the site. Vegetated buffer zones currently being constructed by the RAP at that location will further enhance contaminant immobilization.
- Concentrations of trace organic contaminants in harbour and inflow sediment are largely below detections, or in the range of guidelines, standards and observations that identify the lack of observable biological effects. They are not detected in mussels. PAHs in spottail shiners are comparable to regional values.
- With the exception of the Shipyard property and proximity, contaminants in sediment approach or are below the LEL. In locations where the LEL is marginally exceeded, concentrations are comparable to background values, or biological responses, in terms of community composition and bioassay endpoints, are not statistically different from reference values.
- Sediment samples collected at the Shipyard dry docks and launch basin have concentrations of metals that would be of particular concern if this material

was acting as a source to the harbour. Some chronic toxicity is associated with this sediment

- With the closure of the Collingwood Shipyards in 1986, and the lack of industrial and measurable nonpoint discharges of contaminants to the harbour, sources of contaminants have been controlled. While sediment recovery can be anticipated, the opportunity exists to accelerate natural recovery through the testing of innovative technologies in Collingwood Harbour.

In 1992, concurrent with sediment analyses, the Collingwood Harbour Remedial Action Plan hosted a sediment removal demonstration project to test innovative technologies that could be applied for sediment restoration throughout the Great Lakes Basin. Collingwood Harbour presented a viable location, due to the marginal nature of sediment toxicity, and the relatively small volume of sediment that did not meet both chemical and biological guidelines. In addition, the harbour features a confined disposal facility that has capacity to receive the dredged material.

Approximately 4000 cubic metres of sediment from the CSL dry dock, launch basin and inner harbour were removed using the Pneuma Pump, a system developed in Italy that claims to achieve high solids concentrations by volume in dredge mixture while minimizing the problems of secondary pollution caused by the disturbance of the sediment-water interface. Water depth ranged from 4.1 to 6.3 metres and sediment

depth from 0.4 to 1.8 metres. The maximum pumping capacity was $175 \text{ m}^3.\text{h}^{-1}$.

The pump system is based on a principal of using static water head and compressed air inside cylinders. Each of three cylinders is rapidly filled with slurry by counter pressure due to a hydrostatic head and induced vacuum. When one cylinder has filled, compressed air acts as a piston and the slurry is then forced through a check valve to the discharge pipeline (HSP Inc. 1993). The pipeline was used to transpord dredge mixture form the Pneuma pump to the CDF, and was approximately 1.2 km in lenth, traversing both water and land. A silt curtan located at the north end of each slip was used to confine any possible dredging effects. The silt curtain was constructed of geotextile material, with the top connected to a floating boom and was monitored daily for any indications of damage. Turbidity, suspended solids and total organic carbon concentrations were minimal.

In November 1993, an additional 3000 to 4000 cubic metres of sediment was removed from the northeast zone of the inner harbour, corresponding to the zone of marginal biological impairment.

6 CONCLUSIONS

With the exception of a zone confined to the CSL property, sediment bioassays using sensitive endpoints indicate no observable impacts of harbour sediment on the biota. The elevated lead residues measured in organisms in the 1986 bioassays were not observed in this study. Currently, the significance of metal residues in biota to organism health is not well understood and comparisons of tissue residues with those of organisms from remote locations is one means for evaluating the potential for biological effects. In the case of Collingwood Harbour, tissue residues of contaminants were comparable to concentrations observed in organisms colonizing uncontaminated sediment. In chronic sediment bioassays, no significant mortality occurred, and growth in harbour sediment equalled or exceeded that of controls.

This information, coupled with field observation on native benthic invertebrates, young of the year spottail shiners, sport fish (MOEE/MNR 1992) and introduced mussels provides multiple lines of evidence that support the conclusion that concentrations of biologically available contaminants in Collingwood Harbour sediment are not of toxicological significance.

In the CSL property and proximity, sediment that elicited adverse biological responses, was removed, while demonstrating new innovative technology that could have potential for sediment rehabilitation in more seriously contaminated areas throughout the Great Lakes.

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REFERENCES

Alden III, R.W. and A.J. Butt. 1987. Statistical classification of the toxicity and polynuclear aromatic hydrocarbon contamination of sediments from a highly industrialized seaport. Environ. Toxicol. Chem. 6: 673-684

ASTM 1990. Standard guide for collection, storage, characterization and manipulation of sediments for toxicological testing. 1991 Annual Book of ASTM Standards. Vol. 11.04 E 1391-90: 1105-1119

Brungs, W.A., J.R. Geckler and M. Gast. 1976. Acute and chronic toxicity of copper to the fathead minnow in a surface water of variable quality. Water Research 10: 36-43.

Burton Jr., G.A. 1991. Assessing the toxicity of freshwater sediments. Environ. Toxicol. Chem. 10: 1585-1627.

Campbell, P.G.C., A.G. Lewis, P.M. Chapman, W.K. Fletcher, B.E. Imber, S.N. Luoma, P.M. Stokes, M. Winfrey, 1988. Bioavailability of sediment-bound trace elements. Canadian National Research Council Publication 27694.

Campbell, P.G.C. and A. Tessier. 1989. Geochemistry and bioavailability of trace metals in sediments. in: A. Boudou and F. Ribeyre (Eds.) Aquatic Ecotoxicology: Fundamental Concepts and Methodologies, Vol. 1. Boca Raton, FL: CRC Press. pp. 125-150

Chapman, P.M. 1989. Current approaches to developing sediment quality criteria. Environ. Toxicol. Chem. 8: 589-599.

Chapman, P.M., R.C. Barrick, J.M. Neff and R.C. Swartz. 1987. Four independent approaches to developing sediment quality criteria yield similar values for model containants. Environ. Toxicol. Chem. 6: 723-725.

Chu, K.H., W.M. Cheung, and S.K. Lau. 1990. Trace metals in bivalves and sediment from Tolo Harbour, Hong Kong. Environ. Internat. 16: 31-36.

Davies-Colley, R.J. P.O. Nelson, K.J. Williamson. 1985. Sulfide control of cadmium and copper concentrations in anaerobic estuarine sediments. Mar. Chem. 16: 173-186

Dunbar, P. Director, Department of Parks, Recreation and Culture, Town of Collingwood, Ontario.

Forstner, U. 1987. Sediment -associated contaminants - an overview of scientific bases for developing remedial options. Hydrobiol. 149: 43-52.

Forstner, U. and G.T.W. Wittman. Metal Pollution in the Aquatic Environment. 2nd Ed. Springer Verlag, Berlin. 486 pp.

Heit, M., C.S. Klusek, and K.M. Miller. 1980. Trace element, radionuclide, and polynuclear aromatic hydrocarbon concentrations in Unionidae mussels from northern

Lake George. Environ. Sci. Technol. 14: 465-468

HSP Inc. 1993. Demonstration of Pneuma dredging technology at Collingwood Harbour, Ontario. Report to Environment Canada, Contaminated Sediment Removal Program, Toronto, Ontario. Project No. 1560.

Innes, D.I., B.W. Muncaster, R. Lazar, G.D. Haffner, and P.D.N. Hebert. 1987. Freshwater mussels and biomonitor of organic contaminants. In: Proc. Technology Trans. Conference 8: 1-49. OMOE, Toronto, Ontario

International Joint Commission. 1988. Procedures for the assessment of contaminated sediment problems in the Great Lakes. Report to the Great Lakes Water Quality Board.

Karr, J.R. 1987. Biological monitoring and environmental assessment: a conceptual framework. Environ. Management 11: 249-256.

Kauss, P.B. and Y. S. Hamdy. 1985. Biological monitoring of organochlorine contaminants in the St. Clair and Detroit rivers using introduced clams, *Elliptio complanatus*. J. Great Lakes Res. 11: 247-263

Kauss, P.B. and Y. S. Hamdy. 1991. Polycyclic aromatic hydrocarbons in surficial

sediment and caged mussels of the St. Marys River, 1985. *Hydrogiologia* (in press)

Krantzberg 1990. Sediment bioassay research and development. Report to the Research Advisory Committee, Ontario Ministry of the Environment, PDF03.

Krantzberg, G. 1991. Sediment core chemistry and sediment bioassays, Collingwood Harbour 1989. COA/RAP Technical report.

Krantzberg, G. 1991. Collingwood Harbour Mussel Biomonitoring 1990. Collingwood Harbour Remedial Action Plan Report, Ministry of Environment and Energy, Toronto, Ontario.

Krantzberg, G. and R.C. Bailey. 1983. Report on the revision of MOE guidelines for open water dredge spoils disposal. Report to the Ontario Ministry of the Environment, Water Resources Branch, Ontario.

Krantzberg, G. and Boyd, D. 1992. The biological significance of contaminants in sediment from Hamilton Harbour, Lake Ontario. *Environ. Toxicol. Chem.* 11: 1527-1540.

Krantzberg, G., W. Lammers, L. Sarazin, and M. D'Andrea. 1989. Collingwood harbour Remedial Action Plan Stage I - Environmental COnditions and Problem

Definition. Ontario Ministry of the Environment, Toronto, Ontario.

Krantzberg, G. and P.M. Stokes. 1988. The importance of surface adsorption and pH in metal accumulation by chironomids. Environ. Toxicol. Chem. 7: 653-670.

Lakshmanan, P.T., and P.N.K. Nambisan. 1989. Bioaccumulation and depuration of some trace metals in the mussel, *Perna viridis* (Linnaeus). Bull Environ. Contam. Toxicol. 43: 131-138

Landner, L. 1988. Hazardous chemicals in the environment - some new approaches to advanced assessment. Ambio 17: 360-366

Langston, W.J. and M. Zhou. 1986. Evaluation of the significance of metal-binding proteins in the gastropod *Littorina littorea*. Marine Biology 92: 505-515

Luoma, S.N. 1983. Bioavailability of trace metals to aquatic organisms: A review. Sci. Total Environ. 28: 1-22.

Luoma, G.N. 1989. Can we determine the biological availability of sediment bound trace elements? Hydrobiol. 176/177: 379-396.

Luten, J.B., W. Bouquet, M.M. Burggraaf, A.B. Rauchhaar, and J. Rus. 1986. Trace

metals in mussels (*Mytilus edulis*) from the Waddenzee, Coastal North Sea and the Estuaries of Ems, Western and Eastern Scheldt. Bull. Environ. Contam. Toxicol. 36: 770-777

MOEE (Ontario Ministry of Environment and Energy). 1983. Handbook of analytical methods for environmental samples. Laboratory Services and Applied Research Branch. Toronto, Ontario.

Nalepa, T.F. and P.F. Landrum. 1988. Benthic invertebrate contaminant levels in the Great Lakes: effect, fates, and role in cycling. In: M.S. Evans (Ed.) Toxic Contaminants and Ecosystem Health: A Great Lakes Focus. New York, John Wiley and Sons. pp. 77-102.

Nebeker, A.V., M.A. Cairns, J.H. Gakstater, K.W. Malueg, G.S. Schuytema and D.F. Krawczyk. 1984. Biological methods for determining toxicity of contaminated freshwater sediments to invertebrates. Environ. Toxicol. Chem. 3: 617-630.

Painter, S. 1992. Regional Variability in Sediment Background Metal Concentrations and the Ontario Sediment Quality Guidelines. National Water Research Institute Report, Burlington, Ontario.

Persaud, D., R. Jaagumagi and A. Hayton. 1992. Guidelines for the protection and

management of aquatic sediment quality in Ontario. Report of the Ontario Ministry of the Environment. ISBN 0-7729-9248-7

Phillips, D.J.H. 1979. Trace metals in the common mussel, *Mytilus edulis* (L.) and the algae *Fucus vesiculosus* (L.) from the region of the sound (Öresund). Environ. Pollut. 18: 31-43

Phillips, D.J.H. 1985. Organochlorines and trace metals in greenlipped mussels *Perna viridis* from Hong Kong waters: a test of indicator ability. Mar. Ecol. Prog. Ser. 21: 251-258

Powlesland C. and J. George. 1986. Acute and chronic toxicity of nickel to larvae of Chironomus riparis. Environ. Pollution 42: 47-64.

Pugsley, C.W., P.D.N. Hebert, and P.M. McQuarrie. 1988. Distribution of contaminants in clams and sediments from the Huron-Erie corridor. II- lead and cadmium. J. Great Lakes Res. 14: 356-368.

Reynoldson, T.B., K.E. Day, and R.H. Norris. 1994. Methods for establishing biologically based sediment quality guidelines for freshwater quality management using Benthic Assessment of Sediment (the BEAST). Aust. J. Ecology (in press).

Smith, A.L., R.H. Green, and A. Lutz. 1975. Uptake of mercury by freshwater clams (Family Unionidae). J. Fish. Res. Bd. Canada. 32: 1297-1303.

Suns. L., G. Hitchin, and D. Toner. 1991. Spatial and temporal tends of organochlorine contaminants in spottail shiners (*Notropis hudsonius*) from the Great Lakes and their connecting channels (1975-1988). Ontario Ministry of the Environment, PIBS 1595.

USEPA (US Environmental Protection Agency) 1979. Status assessment of toxic chemicals: Polynuclear aromatic hydrocarbons. EPA-600/2-79-210L Cincinnati, OH.

van de Guchte, C. and C.J. van Leeuwen. Chapter 29, Sediment Pollution. In: H.A.M de Kruijf , D. de Zwart, P.N. Viswanathan, and P.K. Ray. Manual on Aquatic Ecotoxicology. Allied Publishers Private Ltd., New Delhi, India pp. 180-191.

van Veen, H.J., and P.B.M. Stortelder. 1988. Research on contaminated sediment in the Netherlands. in: K. Wolf, W.J. van den Brink, F.J. Colon (eds.) Contaminated Soil '88. Kluwer Acad. Pub. pp. 1263-1275.

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